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An NMR Investigation of the Reactions of Secondary Organoarsines with Symmetric Diarsines and Diphosphines

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Our recent investigations of the reactivity of primary organoarsines, $RAsH_2$, with Me_2AsNMe_2 [1], $Me_2AsAsMe_2$ [2], and cyclic-$(MeAs)_5$ [3] indicate that several facile exchange reactions influence the overall reaction rates and the resulting equilibrium product distributions. This information has been used to design new, efficient, and convenient routes to the high yield syntheses of such compounds as cyclic polyarsines [4].

We were therefore interested in examining the reactions of secondary organoarsines with the corresponding aminoarsines and diarsines. We have reported a NMR study of the reaction of Me_2AsH with Me_2AsNMe_2 [5]. From this study, a new synthetic route to the symmetric diarsine, $Me_2AsAsMe_2$, was devised. In this investigation, we noted that Me_2AsH reacts with $Et_2AsAsEt_2$ to give the unsymmetric diarsine, $Me_2AsAsEt_2$.

There are only a few reports of reactions involving the formation of unsymmetric diarsines [6–9]. Therefore, we have undertaken a systematic study of the $R_2AsH/R'_2AsAsR'_2$ system to determine the mechanism of the overall reaction and to characterize and establish the relative importance of any competing reactions. Here, we report a NMR study of the reactions of R_2AsH with $R'_2AsAsR'_2$ ($R = Me$, $R' = Et$; $R = Et$, $R' = Me$; $R = Me$, $R' = Ph$; $R = Ph$, $R' = Me$) and of Me_2AsH with Et_2PPEt_2. The reactions of Me_2AsH with $(CF_3)_2PP(CF_3)_2$ and of Me_2PH with $(CF_3)_2AsAs(CF_3)_2$ are known to yield mixed phosphinoarsines [7]. The mixed phosphinoarsines have also been obtained by exchange reactions of the corresponding symmetric tetraorganodiarsines and tetraorganodiphosphines [10, 11].

Experimental

Standard high vacuum line techniques and a Vacuum Atmospheres Model-43-Dri Lab equipped with a Model HE-493 Dri-Train were used for the storing and handling of all compounds. Et_2PH was purchased from Strem Chemicals Inc. $Me_2AsAsMe_2$ (60 °C/25 torr) [5], $Et_2AsAsEt_2$ (185 °C) [5], $Ph_2AsAsPh_2$ (melting point (m.p.) 129–130 °C) [12], Me_2AsH (36 °C) [13], Et_2AsH (101–107 °C) [14], Ph_2AsH (160 °C/10 torr) [15], and Et_2PPEt_2 (221–222 °C) [16] were synthesized by standard methods. The NMR tubes were carefully washed in a non-acid media to prevent any possible acid-catalysed exchange.

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Nicolet 300 MHz multinuclear FT NMR spectrometer operating at 300.1, 75.4, and 121.5 MHz, respectively. The ^1H and ^{13}C chemical shifts were measured with respect to tetramethylsilane as an internal reference. The ^{31}P chemical shifts were measured with respect to 85% H_3PO_4 as external reference.

The following reactions of secondary arsines or phosphines with equimolar amounts of symmetric diarsines or diphosphines were studied over the temperature range of −80 to 24 °C as a function of time using ^1H, ^{13}C, and ^{31}P NMR spectroscopy: (1) Me_2AsH with $Et_2AsAsEt_2$ (0.50 mmol); (2) Et_2AsH with $Me_2AsAsMe_2$ (0.50 mmol); (3) Ph_2AsH with $Me_2AsAsMe_2$ (0.50 mmol); (4) Me_2AsH with $Ph_2AsAsPh_2$ (0.25 mmol); (5) Me_2AsH with Et_2PPEt_2 (0.50 mmol), and (6) Et_2PH with $Me_2AsAsMe_2$ (0.50 mmol). Reactions (1)–(6) were carried out in toluene-d_8 solution as reported previously [1, 2]. For the reaction of Et_2PPEt_2 with $Me_2AsAsMe_2$ equimolar amounts of the reactants (0.50 mmol) were dissolved in enough toluene-d_8 at room temperature to give a total solution volume of 4.0 ml. The progress of the reaction was monitored by recording the ^{31}P NMR spectra at selected time intervals until equilibrium was noted.

Results and Discussion

The NMR spectra of the $Me_2AsH/Et_2AsAsEt_2$ system at −80 °C consisted of low intensity peaks assignable to $Me_2AsAsEt_2$ and Et_2AsH and high intensity resonances attributed to the reactants. With increasing temperature, the intensities of the product peaks increased with a concomitant decrease in the intensities of the reactants peaks. At −40 °C, a peak assignable to $Me_2AsAsMe_2$ was observed. After 2 days at 24 °C, the system achieved equilibrium. The ^1H NMR intensity data indicated the presence of 31% $Me_2AsAsEt_2$, 5% $Me_2AsAsMe_2$, 14% $Et_2AsAsEt_2$, 12% Me_2AsH, and 38% Et_2AsH.

The reaction of Et_2AsH with $Me_2AsAsMe_2$ at −80 °C consisted of very low intensity peaks assignable to $Me_2AsAsEt_2$ and Me_2AsH and high intensity resonances corresponding to the reactants. After raising the temperature to −40 °C, the intensities of the product peaks increased and new peaks assignable

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to $Et_2AsAsEt_2$ appeared. After 3 days at 24 °C, the ^1H NMR intensity data indicated an equilibrium mixture containing 30% $Me_2AsAsEt_2$, 16% $Me_2AsAsMe_2$, 4% $Et_2AsAsEt_2$, 37% Me_2AsH, and 13% Et_2AsH.

The NMR spectra of the $Ph_2AsH/Me_2AsAsMe_2$ system indicated no reaction at −80 °C. Very low intensity peaks assignable to $Me_2AsAsPh_2$ and Me_2AsH were noted at −40 °C. At −10 °C, new resonances were also observed due to $Ph_2AsAsPh_2$. The reaction was then followed at 24 °C as a function of time. The ^1H NMR intensity data at equilibrium (after 7 days) indicated the presence of 32% $Me_2AsAsPh_2$, 19% $Me_2AsAsMe_2$, 6% $Ph_2AsAsPh_2$, 12% Ph_2AsH, and 31% Me_2AsH in the reaction mixture.

These results indicate that a change in the substituent (Me, Et, and Ph) bonded to arsenic in the above reaction systems does not affect the final equilibrium distribution of species in the reaction mixture. However, the nature of the substituent does affect the overall rate of reaction. These findings are consistent with our previous observations on the $Me_2AsNR_2/Et_2AsAsEt_2$ and $Et_2AsNR_2/Me_2AsAsMe_2$ systems [6].

The reaction of Me_2AsH with $Ph_2AsAsPh_2$ could only be studied at low concentration (0.25 mmol of each reactants in 4.0 ml solution) and at −10 °C and above due to the low solubility of $Ph_2AsAsPh_2$. The NMR spectra at −10 °C initially showed, in addition to reactant peaks, very low intensity peaks assignable to $Me_2AsAsPh_2$ and Ph_2AsH. The reaction was then followed at 24 °C as a function of time. As the reaction progressed, a new resonance due to $Me_2AsAsMe_2$ was noted. The ^1H NMR equilibrium intensity data (5 days, 24 °C) indicated the presence of 23% $Me_2AsAsPh_2$, 8% $Me_2AsAsMe_2$, 16% $Ph_2AsAsPh_2$, 26% Me_2AsH, and 27% Ph_2AsH in the reaction mixture.

These results suggest that R_2AsH reacts with $R'_2AsAsR'_2$ to yield an unsymmetric diarsine, $R_2AsAsR'_2$, and a secondary arsine, R'_2AsH (eqn. (1)).

$$R_2AsH + R'_2AsAsR'_2 \rightleftharpoons R'_2AsH + R_2AsAsR'_2 \qquad (1)$$

The unsymmetric diarsine then can undergo further reactions involving R_2As– and R'_2As– moiety exchange (eqns. (2) and (3)).

$$2R_2AsAsR'_2 \rightleftharpoons R_2AsAsR_2 + R'_2AsAsR'_2 \qquad (2)$$

$$R_2AsH + R_2AsAsR'_2 \rightleftharpoons R_2AsAsR_2 + R'_2AsH \qquad (3)$$

The symmetrization process represented by eqn. (2) could not be studied directly due to the inability to isolate $R_2AsAsR'_2$. Thus, we have characterized this process by studying the $R_2AsAsR_2/R'_2AsAsR'_2$ systems (R = Me, R' = Et and Ph) [6, 17]. The reaction represented by eqn. (3) can be characterized by studying the corresponding R'_2AsH/R_2AsAsR_2 system. For example, the possibility of the reaction of Et_2AsH with $Me_2AsAsMe_2$ in the $Me_2AsH/Et_2AsAsEt_2$ system was established by independent study of the $Et_2AsH/Me_2AsAsMe_2$ system (see above results).

Due to the lability of the As–As and As–H bonds [1–3, 5, 6, 17], other reactions may also occur in the reaction mixture. For example, R_2AsH can be involved in H– moiety exchange with R'_2AsH. This exchange process has been established previously by independent study of the reaction of Me_2AsD with Et_2AsH in diethylether-d_{10} [18].

This work has also been extended to some systems involving phosphorus analogues. The NMR spectra of an equimolar mixture of Me_2AsH and Et_2PPEt_2 showed no reaction from −80 to −10 °C. At 24 °C, the NMR spectra indicated the formation of Et_2PH and Me_2AsPEt_2. As the reaction progressed, a new peak due to $Me_2AsAsMe_2$ was observed. A disproportionate increase in the intensities of the Et_2PH peaks in comparison to those of Me_2AsPEt_2 was noted. After 18 days, the ^1H and ^{31}P NMR data indicated an equilibrium with total consumption of Me_2AsH to give 52% Et_2PH, 9% Et_2PPEt_2, 12% Me_2AsPEt_2, and 27% $Me_2AsAsMe_2$.

These results suggest that Me_2AsH reacts with Et_2PPEt_2 to give Me_2AsPEt_2 and Et_2PH (eqn. (4)).

$$Me_2AsH + Et_2PPEt_2 \rightleftharpoons Me_2AsPEt_2 + Et_2PH \qquad (4)$$

The phosphinoarsine, Me_2PAsEt_2, then can react with Me_2AsH (eqn. (5)) and be involved in a self-exchange reaction (eqn. (6)).

$$Me_2AsH + Me_2AsPEt_2 \rightleftharpoons Me_2AsAsMe_2 + Et_2PH \qquad (5)$$

$$2Me_2AsPEt_2 \rightleftharpoons Et_2PPEt_2 + Me_2AsAsMe_2 \qquad (6)$$

The disproportionate formation of Et_2PH as compared to that of Me_2AsPEt_2 in the Me_2AsH/Et_2PPEt_2 system can be attributed to the occurrence of competitive reactions of Me_2AsH with Et_2PPEt_2 and Me_2AsPEt_2. Reaction (5) should be favored over (4) since the P–As bond strength appears to be lower than the P–P bond strength [10, 11]. Reactions represented by eqns. (5) and (6) have been characterized by studying the $Et_2PH/Me_2AsAsMe_2$ and $Et_2PPEt_2/Me_2AsAsMe_2$ equilibrium systems (see discussion below) since Me_2AsPEt_2 cannot be isolated from solution [10, 11].

The NMR spectra of the $Et_2PH/Me_2AsAsMe_2$ system indicated no reaction from −80 to −10 °C. The reaction was then followed at 24 °C as a function of time. A slow reaction occurred to yield Me_2AsPEt_2 and Me_2AsH. The ^1H and ^{31}P NMR spectra (21 h) showed the presence of 6% Me_2AsPEt_2, 6% Me_2AsH, 44% Et_2PH, and 44% $Me_2AsAsMe_2$ at equilibrium.

The ^{31}P NMR spectra of an equimolar mixture of Et_2PPEt_2 with $Me_2AsAsMe_2$ at 24 °C in toluene-d_8 indicated a very slow exchange reaction to give an equilibrium mixture (13 days) of Me_2AsPEt_2, Et_2PPEt_2, and $Me_2AsAsMe_2$. An equilibrium constant of 0.22 was obtained from $K = [Me_2AsPEt_2]^2/([Me_4As_2][Et_4P_2])$. This value is consistent with those reported for the $Ph_2PPPh_2/Ph_2AsAsPh_2$ (0.37) [10] and $Me_2PPMe_2/Me_2AsAsMe_2$ (0.26) systems [11].

The results of our present study indicate that unsymmetric diarsines and phosphinoarsines are formed in the reactions of secondary arsines with symmetric diarsines and diphosphines, respectively. The overall reaction sequences are complex, since additional exchange reactions involving the R_2As-, R'_2As-, and R'_2P- species can be present. These competing reactions influence the rate of formation and relative yields of unsymmetric diarsines and phosphinoarsines. The fact that Me_2AsH readily reacts with $Et_2AsAsEt_2$ at −80 °C, while no reaction occurs upto −10 °C with Et_2PPEt_2 suggests that the As–As bond is more labile toward reaction with the As–H bond than with the P–P bond. The $>AsH/>AsAs<$ and $>AsH/>PP<$ systems are being studied further to determine the electronic and steric effects that various substituents have on the course of the reaction sequence.

Supplementary Material

^1H, ^{13}C, and ^{31}P NMR spectral data [δ, ppm] in toluene-d_8 solution at 24 °C were independently determined on synthesized compounds that were identified in the reaction mixtures. These data are available from the authors on request.

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