

## 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-( $MeAs$ )<sub>3</sub> [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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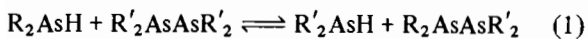
to  $\text{Et}_2\text{AsAsEt}_2$  appeared. After 3 days at  $24^\circ\text{C}$ , the  $^1\text{H}$  NMR intensity data indicated an equilibrium mixture containing 30%  $\text{Me}_2\text{AsAsEt}_2$ , 16%  $\text{Me}_2\text{AsAsMe}_2$ , 4%  $\text{Et}_2\text{AsAsEt}_2$ , 37%  $\text{Me}_2\text{AsH}$ , and 13%  $\text{Et}_2\text{AsH}$ .

The NMR spectra of the  $\text{Ph}_2\text{AsH}/\text{Me}_2\text{AsAsMe}_2$  system indicated no reaction at  $-80^\circ\text{C}$ . Very low intensity peaks assignable to  $\text{Me}_2\text{AsAsPh}_2$  and  $\text{Me}_2\text{AsH}$  were noted at  $-40^\circ\text{C}$ . At  $-10^\circ\text{C}$ , new resonances were also observed due to  $\text{Ph}_2\text{AsAsPh}_2$ . The reaction was then followed at  $24^\circ\text{C}$  as a function of time. The  $^1\text{H}$  NMR intensity data at equilibrium (after 7 days) indicated the presence of 32%  $\text{Me}_2\text{AsAsPh}_2$ , 19%  $\text{Me}_2\text{AsAsMe}_2$ , 6%  $\text{Ph}_2\text{AsAsPh}_2$ , 12%  $\text{Ph}_2\text{AsH}$ , and 31%  $\text{Me}_2\text{AsH}$  in the reaction mixture.

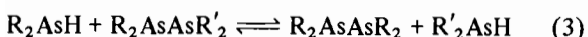
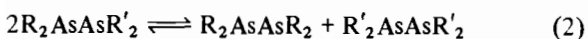
These results indicate that a change in the substituent (Me, Et, and Ph) bonded to arsenic in the above reaction systems does not affect the final equilibrium distribution of species in the reaction mixture. However, the nature of the substituent does affect the overall rate of reaction. These findings are consistent with our previous observations on the  $\text{Me}_2\text{AsNR}_2/\text{Et}_2\text{AsAsEt}_2$  and  $\text{Et}_2\text{AsNR}_2/\text{Me}_2\text{AsAsMe}_2$  systems [6].

The reaction of  $\text{Me}_2\text{AsH}$  with  $\text{Ph}_2\text{AsAsPh}_2$  could only be studied at low concentration (0.25 mmol of each reactants in 4.0 ml solution) and at  $-10^\circ\text{C}$  and above due to the low solubility of  $\text{Ph}_2\text{AsAsPh}_2$ . The NMR spectra at  $-10^\circ\text{C}$  initially showed, in addition to reactant peaks, very low intensity peaks assignable to  $\text{Me}_2\text{AsAsPh}_2$  and  $\text{Ph}_2\text{AsH}$ . The reaction was then followed at  $24^\circ\text{C}$  as a function of time. As the reaction progressed, a new resonance due to  $\text{Me}_2\text{AsAsMe}_2$  was noted. The  $^1\text{H}$  NMR equilibrium intensity data (5 days,  $24^\circ\text{C}$ ) indicated the presence of 23%  $\text{Me}_2\text{AsAsPh}_2$ , 8%  $\text{Me}_2\text{AsAsMe}_2$ , 16%  $\text{Ph}_2\text{AsAsPh}_2$ , 26%  $\text{Me}_2\text{AsH}$ , and 27%  $\text{Ph}_2\text{AsH}$  in the reaction mixture.

These results suggest that  $\text{R}_2\text{AsH}$  reacts with  $\text{R}'_2\text{AsAsR}'_2$  to yield an unsymmetric diarsine,  $\text{R}_2\text{AsAsR}'_2$ , and a secondary arsine,  $\text{R}'_2\text{AsH}$  (eqn. (1)).



The unsymmetric diarsine then can undergo further reactions involving  $\text{R}_2\text{As}-$  and  $\text{R}'_2\text{As}-$  moiety exchange (eqns. (2) and (3)).



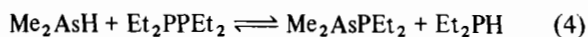
The symmetrization process represented by eqn. (2) could not be studied directly due to the inability to isolate  $\text{R}_2\text{AsAsR}'_2$ . Thus, we have characterized this process by studying the  $\text{R}_2\text{AsAsR}_2/\text{R}'_2\text{AsAsR}'_2$  systems ( $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Et}$  and  $\text{Ph}$ ) [6, 17]. The reaction represented by eqn. (3) can be characterized by studying the corresponding  $\text{R}'_2\text{AsH}/\text{R}_2\text{AsAsR}_2$  system. For example, the possibility of the reaction of  $\text{Et}_2\text{AsH}$  with  $\text{Me}_2\text{AsAsMe}_2$  in the  $\text{Me}_2\text{AsH}/$

$\text{Et}_2\text{AsAsEt}_2$  system was established by independent study of the  $\text{Et}_2\text{AsH}/\text{Me}_2\text{AsAsMe}_2$  system (see above results).

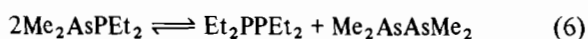
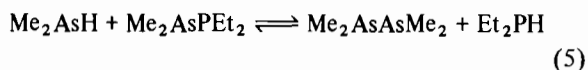
Due to the lability of the As-As and As-H bonds [1-3, 5, 6, 17], other reactions may also occur in the reaction mixture. For example,  $\text{R}_2\text{AsH}$  can be involved in H- moiety exchange with  $\text{R}'_2\text{AsH}$ . This exchange process has been established previously by independent study of the reaction of  $\text{Me}_2\text{AsD}$  with  $\text{Et}_2\text{AsH}$  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  $\text{Me}_2\text{AsH}$  and  $\text{Et}_2\text{PPEt}_2$  showed no reaction from  $-80$  to  $-10^\circ\text{C}$ . At  $24^\circ\text{C}$ , the NMR spectra indicated the formation of  $\text{Et}_2\text{PH}$  and  $\text{Me}_2\text{AsPET}_2$ . As the reaction progressed, a new peak due to  $\text{Me}_2\text{AsAsMe}_2$  was observed. A disproportionate increase in the intensities of the  $\text{Et}_2\text{PH}$  peaks in comparison to those of  $\text{Me}_2\text{AsPET}_2$  was noted. After 18 days, the  $^1\text{H}$  and  $^{31}\text{P}$  NMR data indicated an equilibrium with total consumption of  $\text{Me}_2\text{AsH}$  to give 52%  $\text{Et}_2\text{PH}$ , 9%  $\text{Et}_2\text{PPEt}_2$ , 12%  $\text{Me}_2\text{AsPET}_2$ , and 27%  $\text{Me}_2\text{AsAsMe}_2$ .

These results suggest that  $\text{Me}_2\text{AsH}$  reacts with  $\text{Et}_2\text{PPEt}_2$  to give  $\text{Me}_2\text{AsPET}_2$  and  $\text{Et}_2\text{PH}$  (eqn. (4)).



The phosphinoarsine,  $\text{Me}_2\text{PASet}_2$ , then can react with  $\text{Me}_2\text{AsH}$  (eqn. (5)) and be involved in a self-exchange reaction (eqn. (6)).



The disproportionate formation of  $\text{Et}_2\text{PH}$  as compared to that of  $\text{Me}_2\text{AsPET}_2$  in the  $\text{Me}_2\text{AsH}/\text{Et}_2\text{PPEt}_2$  system can be attributed to the occurrence of competitive reactions of  $\text{Me}_2\text{AsH}$  with  $\text{Et}_2\text{PPEt}_2$  and  $\text{Me}_2\text{AsPET}_2$ . 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  $\text{Et}_2\text{PH}/\text{Me}_2\text{AsAsMe}_2$  and  $\text{Et}_2\text{PPEt}_2/\text{Me}_2\text{AsAsMe}_2$  equilibrium systems (see discussion below) since  $\text{Me}_2\text{AsPET}_2$  cannot be isolated from solution [10, 11].

The NMR spectra of the  $\text{Et}_2\text{PH}/\text{Me}_2\text{AsAsMe}_2$  system indicated no reaction from  $-80$  to  $-10^\circ\text{C}$ . The reaction was then followed at  $24^\circ\text{C}$  as a function of time. A slow reaction occurred to yield  $\text{Me}_2\text{AsPET}_2$  and  $\text{Me}_2\text{AsH}$ . The  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra (21 h) showed the presence of 6%  $\text{Me}_2\text{AsPET}_2$ , 6%  $\text{Me}_2\text{AsH}$ , 44%  $\text{Et}_2\text{PH}$ , and 44%  $\text{Me}_2\text{AsAsMe}_2$  at equilibrium.

The  $^{31}\text{P}$  NMR spectra of an equimolar mixture of  $\text{Et}_2\text{PPEt}_2$  with  $\text{Me}_2\text{AsAsMe}_2$  at  $24^\circ\text{C}$  in toluene- $d_8$  indicated a very slow exchange reaction to give an

equilibrium mixture (13 days) of  $\text{Me}_2\text{AsPEt}_2$ ,  $\text{Et}_2\text{PPEt}_2$ , and  $\text{Me}_2\text{AsAsMe}_2$ . An equilibrium constant of 0.22 was obtained from  $K = [\text{Me}_2\text{AsPEt}_2]^2 / ([\text{Me}_4\text{As}_2][\text{Et}_4\text{P}_2])$ . This value is consistent with those reported for the  $\text{Ph}_2\text{PPPh}_2/\text{Ph}_2\text{AsAsPh}_2$  (0.37) [10] and  $\text{Me}_2\text{PPMe}_2/\text{Me}_2\text{AsAsMe}_2$  (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  $\text{R}_2\text{As}-$ ,  $\text{R}'_2\text{As}-$ , and  $\text{R}'_2\text{P}-$  species can be present. These competing reactions influence the rate of formation and relative yields of unsymmetric diarsines and phosphinoarsines. The fact that  $\text{Me}_2\text{AsH}$  readily reacts with  $\text{Et}_2\text{AsAsEt}_2$  at  $-80^\circ\text{C}$ , while no reaction occurs upto  $-10^\circ\text{C}$  with  $\text{Et}_2\text{PPEt}_2$  suggests that the As-As bond is more labile toward reaction with the As-H bond than with the P-P bond. The  $>\text{AsH}/>\text{AsAs}<$  and  $>\text{AsH}/>\text{PP}<$  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

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectral data [ $\delta$ , ppm] in toluene- $d_8$  solution at  $24^\circ\text{C}$  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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### References

- 1 V. K. Gupta, L. K. Krannich and C. L. Watkins, *Inorg. Chim. Acta*, **126**, 173 (1987).
- 2 V. K. Gupta, L. K. Krannich and C. L. Watkins, *Inorg. Chim. Acta*, **132**, 163 (1987).
- 3 V. K. Gupta, L. K. Krannich and C. L. Watkins, *Inorg. Chem.*, **26**, 1638 (1987).
- 4 V. K. Gupta, L. K. Krannich and C. L. Watkins, *Synth. React. Inorg. Met-Org. Chem.*, **17**, 501 (1987).
- 5 V. K. Gupta, L. K. Krannich and C. L. Watkins, *Inorg. Chem.*, **25**, 2553 (1986).
- 6 V. K. Gupta, L. K. Krannich and C. L. Watkins, *Polyhedron*, **6**, 1229 (1987).
- 7 R. G. Cavell and R. C. Dobbie, *J. Chem. Soc. A*, 1406 (1968).
- 8 R. L. Grant and A. B. Burg, *J. Am. Chem. Soc.*, **84**, 1834 (1962).
- 9 K. Issleib and K. Krech, *Chem. Ber.*, **98**, 1093 (1965).
- 10 A. Belforte, F. Calderazzo, A. Morvillo, G. Pelizzi and D. Vitali, *Inorg. Chem.*, **23**, 1504 (1984).
- 11 A. J. Ashe, III and E. G. Ludwig, Jr., *J. Organomet. Chem.*, **303**, 197 (1986).
- 12 L. K. Krannich and H. H. Sisler, *Inorg. Chem.*, **8**, 1032 (1969).
- 13 W. M. Dehn and B. B. Wilcox, *Am. Chem. J.*, **35**, 1 (1906).
- 14 A. Tzschach and W. Lange, *Z. Anorg. Allg. Chem.*, **326**, 280 (1960).
- 15 E. Wiberg and K. Modritzer, *Z. Naturforsch. Anorg. Chem.*, **126**, 127 (1957).
- 16 K. Issleib and W. Seidel, *Chem. Ber.*, **92**, 2681 (1959).
- 17 V. K. Gupta, L. K. Krannich and C. L. Watkins, *J. Organomet. Chem.*, submitted for publication.
- 18 W. R. Cullen and W. R. Leeder, *Can. J. Chem.*, **48**, 3757 (1970).