

An Nmr Study of the Reactions of Primary Alkylphosphines, Arsines and Stibines with Disulfur Dichloride

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We have previously observed many similarities between the chemistry of the sulfur atom and the heavier primary organopnictogen (RE<) moieties (E = P, As or Sb) [1]. Of particular interest has been the propensity of both moieties under similar chemical conditions to form a broad variety of homoatomic catenate structures. In order to more directly assess the validity of this observation, we have studied a series of competitive catenation reactions involving the formation of $(\text{CH}_3\text{E})_x$ and S_x through the treatment of primary alkylhydrides, CH_3EH_2 , with S_2Cl_2 . Fluck and Reinisch found that $\text{C}_6\text{H}_5\text{PH}_2$ and S_2Cl_2 combine to form a heteroatomic four-membered ring, $(\text{C}_6\text{H}_5\text{PS}_2)_2$, and HCl [2]. Reactions of methylamine with S_2Cl_2 over a range of initial reactant molar ratios lead to several heterocyclic products containing the S-N linkage [3]. Additional motivation for the present study is provided by the substantial current interest in S-N polymers and efforts directed toward the preparation of isoelectronic analogs [4]. In none of the reactions we now report, however, is any evidence seen for the formation of heteroatomic catenate structures.

This project also represents the first comparative reactivity study of alkylhydrides of the elements, phosphorus, arsenic and antimony (the instability of bismuth hydrides [5] precluded their inclusion).

Experimental

Methylphosphine [6], methylarsine [7] and ethylarsine [7] were prepared by literature methods, and methylstibine was obtained by the LiAlH_4 reduction of methylchlorostibine in di-n-butylether [8]. All reagents were found spectroscopically pure (IR, MS and PMR).

Solutions of varying molar ratios of the primary alkyl hydrides (REH_2 , E = P, As or Sb) and disulfur dichloride, S_2Cl_2 (freshly distilled from sulfur) were combined in benzene (freshly distilled from sodium)

as approximately 10% solutions and sealed in medium-wall 5 mm o.d. nmr tubes. The hydrides were added by direct vacuum-line distillation into the tube and all solutions were thoroughly degassed by repetitive freeze-pump-thaw cycles. A small quantity of a chemical shift and integration standard was also added (either TMS or cyclohexane). The rapid formation of considerable quantities of solid polymethylpolyarsine in reactions in which CH_3AsH_2 was in excess required that the tubes be thawed slowly while undergoing slow (5 rpm), end-over-end rotation to prevent formation of a solid plug. All reactions that did not rapidly reach a static state based upon periodic nmr monitoring were thermostated at $60.0 \pm 0.5^\circ\text{C}$.

Nmr spectra were recorded on a Perkin-Elmer R20B spectrometer. All chemical shifts are TMS = 0.00 δ , and coupling constants are the average of at least three scans at minimum calibrated sweep widths. Reported chemical shifts of mixture components all compare within acceptable limits to benzene solutions of the individual compounds.

Results and Discussion

For all of the hydrides studied, CH_3PH_2 , CH_3AsH_2 , $\text{C}_2\text{H}_5\text{AsH}_2$ and CH_3SbH_2 , extensive transfer of chlorine from sulfur to pnictogen occurs immediately upon thawing the benzene solutions. The golden color imparted to the initial solutions by S_2Cl_2 is also immediately discharged when the molar quantity of S_2Cl_2 is equal to or less than that of the hydride.

CH_3PH_2

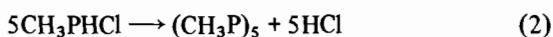
At a 2:1 molar ratio of CH_3PH_2 and S_2Cl_2 (1.10 mmol CH_3PH_2 /0.55 mmol S_2Cl_2) after 24 hr at 60° , 0.75 mmol CH_3PHCl , 0.03 mmol $(\text{CH}_3\text{P})_5$, 0.20 mmol H_2S and 0.27 mmol unreacted CH_3PH_2 were identified by nmr chemical shift and quantitatively determined by spectral integration by comparison to a known quantity of internal standard; these values did not change during the next 18 months. Approximately equal molar quantities of hydridic H and Cl are unaccounted for by mass balance and may be attributed to HCl whose presence is additionally suggested by the small amount of white precipitate which possessed dissociation pressures in accord with methylphosphonium chloride, and by the spectral form of unreacted CH_3PH_2 . By rapid exchange of hydridic H on CH_3PH_2 with HCl (eq. 1) the methyl group appears as a slightly broadened (2Hz half-height linewidth) spin decoupled singlet (0.85 δ).



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Essentially similar spectral features are found in our previously reported spectra of CH_3AsH_2 in the presence of hydrogen halides [9, 10]. No signal is seen for either HCl or the phosphorus-bonded protons on CH_3PH_2 due to their extreme broadening. A small sulfur deficit is also shown by mass balance which can be accounted for by the amount of monoclinic S_8 (mp = 119.5 °C) removed by filtration. No CH_3PCL_2 is found.

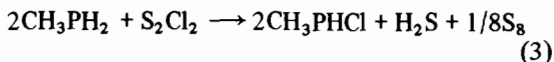
Methylchlorophosphine (CH_3PHCl) has not been previously reported. The arsenic analog, CH_3AsHCl , while stable in equilibrium with CH_3AsH_2 and CH_3AsCl_2 , immediately loses HCl on isolation to form various liquid and solid modifications of homoatomic catenated polymethylpolyarsine [9]. CH_3PHCl behaves similarly except that the only catenate structure found on decomposition is the cyclooligomer, $(\text{CH}_3\text{P})_5$, eq. 2.



Several features of the pmr spectrum of CH_3PHCl are noteworthy. The first order spectrum is characterized by $\delta\text{CH}_3 = 1.48$ (doublet of doublets), $\delta\text{PH} = 5.10$ (doublet of quartets), $^1\text{J}_{\text{PH}} = 241.2\text{Hz}$, $^2\text{J}_{\text{PCH}} = 14.7\text{Hz}$ and $^3\text{J}_{\text{PCH}} = 3.4\text{Hz}$. Both δPH [11] and $^1\text{J}_{\text{PH}}$ [12] are the largest values for these parameters we are aware of for a three-bonded phosphorus compound. No evidence for a rapid proton-proton exchange analogous to that found for CH_3PH_2 is observed for CH_3PHCl due presumably to the diminished hydridic character of the phosphorus-bonded hydrogen in CH_3PHCl .

H_2S appears as a singlet whose position is somewhat concentration dependent (0.3–0.4 δ), and $(\text{CH}_3\text{P})_5$ as a broad singlet (due to extreme spectral complexity) at 1.12 δ . Seel *et al.* report that $(\text{CH}_3\text{P})_5$ (in a mixture with CH_3PF_2 and CH_3PF_4) appears as a broad singlet at about 1.5 δ [13].

The observed events can be summarized in eq. 1–3, occurring in reversed order.



At an initial 1:1 ratio of CH_3PH_2 and S_2Cl_2 , no CH_3PHCl or $(\text{CH}_3\text{P})_5$ and only a trace of H_2S (after 24 hours) is found. At this time the only major products are CH_3PCL_2 ($\delta\text{CH}_3 = 1.90$, $^2\text{J}_{\text{PCH}} = 14.5\text{Hz}$) and H_2S_2 ($\delta\text{H} = 1.89$) [14], *i.e.*, eq. 4:

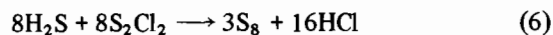


During the next 120 days, the quantity of H_2S_2 decreases by about 1/3, and is accompanied by an increase in H_2S and the initiation of the precipitation of S_8 according to the disproportionation shown in eq. 5 [15].



The sole presence of S_8 as a catenated end product can be attributed to the absence of CH_3PHCl which appears to be the necessary precursor (in this system) to the cyclopolyphosphine.

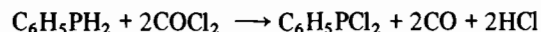
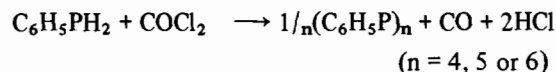
At a 1:2 ratio of CH_3PH_2 and S_2Cl_2 , no H_2S or H_2S_2 is found. Instead, HCl ($\delta\text{HCl} = 0.20$), CH_3PCL_2 and S_8 are obtained. In this case the solution retains the golden color of unreacted S_2Cl_2 . Thus hydrogen sulfide (or hydrogen polysulfide) formed on H/Cl exchange of S_2Cl_2 with CH_3PH_2 would be consumed by excess S_2Cl_2 to produce S_8 and HCl, eq. 6 [16].



Equation 6, like many of the earlier shown equations are clearly not meant to represent elementary steps; eq. 6 undoubtedly involves the intermediate formation of a wide variety of *catena* and *cyclo* polysulfur species.

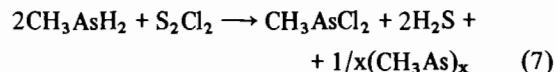
There is no evidence for the formation of any compound at any initial molar ratio containing a P–S bond, in contrast to the reaction of $\text{C}_6\text{H}_5\text{PH}_2$ and S_2Cl_2 [2] (see introduction).

The outcome of the CH_3PH_2 reactions bears striking resemblances to the molar ratio dependent reactions of $\text{C}_6\text{H}_5\text{PH}_2$ with phosgene [17].

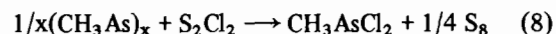


CH_3AsH_2

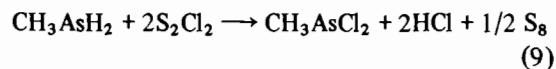
At a 2:1 molar ratio, 0.50 mmol CH_3AsH_2 and 0.25 mmol S_2Cl_2 , CH_3AsCl_2 , H_2S and the purple solid modification of $(\text{CH}_3\text{As})_x$ [10] are found. In contrast to the reaction of CH_3PH_2 at the same molar ratio, no unreacted CH_3AsH_2 , CH_3AsHCl or soluble forms of $(\text{CH}_3\text{As})_x$, *e.g.*, arsenomethane $(\text{CH}_3\text{As})_5$, are in evidence. The products quantitatively satisfy the stoichiometry of eq. 7.



At the opposite molar ratio (0.25 mmol CH_3AsH_2 , 0.50 mmol S_2Cl_2), some $(\text{CH}_3\text{As})_x$ forms initially but disappears quickly if the reaction tube is agitated while it thaws; this disappearance of $(\text{CH}_3\text{As})_x$ under conditions where unreacted S_2Cl_2 remains is explainable by the attack of S_2Cl_2 on the arsenic polymer, eq. 8.



The overall reaction at this molar ratio can then be represented as

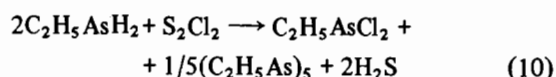


A quantity of monoclinic S_8 satisfying eq. 9 is retrieved from this reaction.

At molar ratios between 2:1 and 1:2 various mixtures of the products shown in eq. 7 and 9 are observed.

$C_2H_5AsH_2$

A single ratio of $C_2H_5AsH_2$ and S_2Cl_2 of 2:1 (1.0 mmol $C_2H_5AsH_2$, 0.5 mmol S_2Cl_2) was studied. In confirmation of our earlier studies, the substitution of ethyl for methyl precludes the formation of any solid polyarsines for what appear to be steric reasons [1]. The nmr spectrum shows only the presence of $(C_2H_5As)_5$, $C_2H_5AsCl_2$ and H_2S . Although the overlapping and complex nmr signals of $(C_2H_5As)_5$ and $C_2H_5AsCl_2$ precluded obtaining accurate integration data, the approximate areas strongly suggest that the reaction progresses analogously to eq. 7, except that the solid polymeric catenate has been replaced by a cyclopentamer:



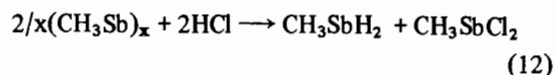
CH_3SbH_2 [18]

At both 2:1 and 1:1 ratios of CH_3SbH_2 and S_2Cl_2 rapid reactions occur producing CH_3SbCl_2 , H_2S and a lustrous pale green solid with a metallic sheen which analyzes successfully for $(CH_3Sb)_x$ (required: 2.19% H, 8.77% C, 89.04% Sb; found: 2.17% H, 8.56% C, 88.94% Sb). This solid is believed to be the first example of the antimony analog of the $(CH_3As)_x$ ladder polymer; a confirmatory X-ray structural characterization awaits the preparation of crystals of adequate size. The solid is, like the arsenic analog [10], insoluble in all tested solvents, indefinitely air stable, and produces a mass spectrum whose highest found peak corresponds to a pentameric composition. Since heating to 230 °C was required to obtain a suitable mass spectrum, the observed pentamer ion suggests only that extensive polymer decomposition occurred.

Unlike the reactions with CH_3PH_2 and CH_3AsH_2 , long-term changes in the nmr spectra of the CH_3SbH_2 reactions caused by slow reactions over a period of 500 days at 60 °C are seen. At both initial ratios, slow growth of a singlet at 0.83δ is tentatively identified as thioantimonymethane (methylstibine sulfide), CH_3SbS , which Morgan and Davies [19] report to be a moderately benzene soluble yellow solid (m.p. 70 °C) of unknown complexity prepared from CH_3SbCl_2 and H_2S (both reagents are present in our reaction mixtures and decrease in concentration in quantities approximated by eq. 11).



No evidence, however, is seen for the presence of HCl; this may be explained by an Sb–Sb bond attack by HCl on $(CH_3Sb)_x$, eq. 12 [20].



The CH_3SbH_2 produced in eq. 12 could then combine with several of the abundant mixture components. Despite the rapid thermal decomposition of CH_3SbH_2 (a 5 mmol sample completely degrades to $(CH_3Sb)_x$ and H_2 *in vacuo* in 30 min at 20 °C), no non-condensable (at –196 °C) gases are produced in these reactions.

After 500 days, all of the lustrous green solid form of $(CH_3Sb)_x$ has given way to a complex black, solid mixture showing lower C and H percentages and variable S percentage (5 – 15%). It is likely a mixture of metallic Sb, Sb_2S_3 and non-crystalline forms of $(CH_3Sb)_x$. A sharp singlet at 1.70δ, which initially appears after about 30 days, may be dimethylsulfide and would account for the methyl groups lost on Sb–C bond cleavage.

Comments

Alkyl substituted heteroatomic S–E (E = P, As or Sb) bonded catenates (either linear or cyclic) cannot be obtained by combinations of hydrides and chlorides of these elements. Rather, condensation to form homoatomic species is favored: pnictogen–pnictogen bonded forms in pnictogen-rich systems, and S_8 in sulfur-rich systems. Exclusivity is also seen in the arsenic and antimony systems; in neither of these cases did homoatomic catenates of both pnictogen and sulfur persistently coexist.

Acknowledgements

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