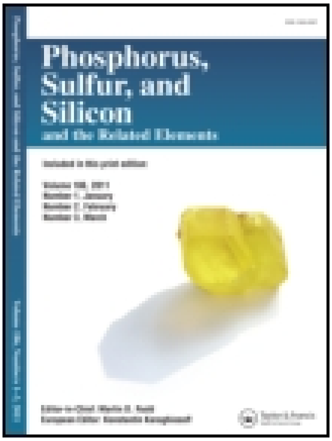

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FISSION OF As-As BONDS IN ELEMENTAL ARSENIC BY ALKALI METALS IN LIQUID AMMONIA. PREPARATION OF DIALKYL AND TRIALKYL ARSINES

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FISSION OF As-As BONDS IN ELEMENTAL ARSENIC BY ALKALI METALS IN LIQUID AMMONIA. PREPARATION OF DIALKYL AND TRIALKYL ARSINES

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Suspensions of alkali arsenides $MAsH_2$ (M= Li, Na or K) in liquid ammonia have been prepared by dropwise addition of *t*-butyl alcohol (2 equiv.) to a mixture of dissolved metal (3 equiv.) and powdered arsenic. Subsequent reaction with an alkyl halide gave dialkyl arsines in good yields as main products in the cases of $LiAsH_2$ and $NaAsH_2$, and trialkyl arsines in excellent yields in the case of $KAsH_2$.

Keywords: Arsines-acidity of; deprotonation of; Alkali metal arsenides-alkylation of; alkali *t*-butoxides-in deprotonation of arsines

INTRODUCTION

Recently, it has been shown that fission of P-P bonds in elemental phosphorus can be achieved by *t*-butyl alcohol-assisted reaction of red or white phosphorus with lithium in liquid ammonia[1]. The lithium phosphide $LiPH_2$ could be alkylated *in situ* to afford monoalkyl phosphines RPH_2 as main products. There are a few reports on reactions of elemental arsenicum with alkali metals in liquid ammonia (in the absence of other reagents)[2]. The experimental information in these papers does not allow to

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conclude whether the reactions proceeded to completion in the ammoniacal solutions or when practically all ammonia had evaporated. The reactions described were not aimed at preparation of organoarsenic compounds.

We here report that arsenic (black modification) can be converted into alkali metal arsenides under conditions similar to those applied to prepare phosphides. Subsequent reaction with alkyl halides affords dialkyl arsines or trialkyl arsines as main products in good to excellent yields.

RESULT AND DISCUSSION

As in the case of the reactions between elemental phosphorus and alkali metals in liquid ammonia[1]. we assume that the complete degradation of the arsenic molecule under the applied conditions is not possible without the assistance of a proton donor. We assume that with two mol equivalents of *t*-butyl alcohol monoalkali arsenide is formed according to the following overall equation:

$$\mathrm{As} + 3\ \mathrm{M} + 2\,t\text{-}\mathrm{BuOH} \longrightarrow \mathrm{MAsH_2} + 2\,t\text{-}\mathrm{BuOM}$$

Alkali *t*-butoxides, especially *t*-BuOK (addition of triphenylmethane to a solution of this base in liquid ammonia gives a pink solution containing triphenylmethylpotassium[3]) are rather strong bases. They may deprotonate initially formed primary arsines (presumably more acidic than phosphines) or even secondary arsines during the alkylation operation. The formation of dihexyl arsine in the reaction As + 3 Li + 2 *t*-BuOH + hexyl bromide may be explained by assuming deprotonation of the initial primary arsine by *t*-BuOLi and subsequent further alkylation to give dihexyl arsine:

$$\mathrm{LiAsH_2} + \mathrm{C_6H_{13}Br} \longrightarrow \mathrm{C_6H_{13}AsH_2}$$
$$\mathrm{C_6H_{13}AsH_2} + t\text{-}\mathrm{BuOLi} \rightleftharpoons \mathrm{C_6H_{13}AsHLi} + t\text{-}\mathrm{BuOH}$$
$$\mathrm{C_6H_{13}AsHLi} + \mathrm{C_6H_{13}Br} \rightarrow (\mathrm{C_6H_{13}})_2\mathrm{AsH}$$

The considerable amounts of trihexyl arsine obtained from the reaction As + 3 Na + 2 *t*-BuOH + hexyl bromide and exclusive formation of tripropyl arsine from the reaction 3 K + As + 2 *t*-BuOH + propyl bromide may result from similar sequences of alternating alkylation and deprotonation. The efficiency of the *t*-alkoxides (in terms of equilibrium concentrations of arsenide) increases in the order *t*-BuOLi<*t*-BuONa<*t*-BuOK[4]. In a separate experiment we obtained trihexyl arsine in excellent yield by slowly adding hexyl bromide to a mixture of dihexyl arsine and 200 mol% excess of *t*-BuONa in liquid ammonia. Alternatively, the dialkyl and trialkyl arsines may be the result from transmetallation and subsequent alkylation, e.g.:

$$RAsH_2 + MAsH_2 \rightarrow RAsHM + AsH_3$$
$$RAsHM + RBr \rightarrow R_2AsH$$

The arsine, AsH_3, formed in the transmetallation may be recovered as alkali arsenide $MAsH_2$ by reaction with *t*-butoxide.

EXPERIMENTAL

Freshly powdered arsenic (0.20 mol) was cautiously added to a stirred solution of the alkali metal (0.60 mol) in 600 ml of liquid ammonia in a 1-L round-bottomed, three-necked flask equipped with a nitrogen inlet, an efficient mechanical stirrer and an outlet. Small amounts of dry ether were occasionally added in the case of serious foaming (especially during the addition to the solution of *potassium*). After 45 min the deep-blue colour of the dissolved metal was still present. Dropwise addition of a mixture of *t*-butyl alcohol (0.40 mol, dried by distillation from potassium) and tetrahydrofuran (50 ml) was then started, while nitrogen (200 ml/min) was passed through the flask. After completion of the addition (taking 45 min) the colour of the reaction mixture changed to dark-green or -after stirring for an additional 15 to 20 min-yellowish-and suspended material became visible. Cautious, portionwise addition (an outlet with a wider opening was used) of n-hexyl or n-propyl bromide was then started. The reactions were very vigorous during the greater part of the addition period, making compensation with 200 to 250 ml of ammonia for the loss due to evaporation necessary. The addition was stopped (after about half an hour) when the intensity of the flow of ammonia from the outlet had decreased considerably and the yellow colour of the reaction mixture had disappeared. The amount of hexyl bromide added in the cases of $LiAsH_2$ and $NaAsH_2$ was 0.4 and 0.6 mol, respectively. After an additional 1 h stirring was stopped and the ammonia was allowed to evaporate overnight while nitrogen was passed through the flask at a rate of 100 to 150 ml/min. After dissolution of the salt in 200 ml of deaerated water, the mixture was extracted three times with a 1:1 mixture of diethyl ether and pentane. After drying the extracts over $MgSO_4$ (all operations during work-up and isolation were scrupulously carried out under nitrogen) and removal of the solvents under reduced pressure, the remainig liquid was carefully distilled through a 25-cm Vigreux column. The following results were obtained.

3 Li + As + 2 *t*-BuOH + *n*-hexyl bromide: 32 g $(C_6H_{13})_2AsH$ (63 % based on As), b.p. 95°C/0.6 Torr, $n^{20}{}_D$ 1.4737, purity (G.C, Varian 3400, column DB-5, 15 m, 0.50 mm internal diameter, 1.5 micrometer film, FID) 99%; ^{1}H-NMR($CDCl_3$) 0.89; 1.29; 1.52; 1.68; 2.47 ppm; ^{13}C-NMR 31.50; 31.00; 29.22; 22.58; 18.44; 14.04 ppm; exact mass calcd. 246.1329, found 246.1380. 3 Na + As + 2 *t*-BuOH + *n*-hexyl bromide: $(C_6H_{13})_2AsH$, 31 g (62% yield) and $(C_6H_{13})_3As$, 15 g (23 %), b.p. 135°C/0.5 Torr, $n^{20}{}_D$ 1.4728, purity (G.C.) 97.5%; ^{1}H-NMR 1.35; 0.88 ppm; ^{13}C-NMR 31.67; 31.59; 26.93; 25.30; 22.59; 14.04 ppm; exact mass calcd. 330.2268, found 330.2436.

3 K + As + 2 *t*-BuOH + *n*- propyl bromide: $(C_3H_7)_3As$, 36 g (90% yield), b.p. 90–92°C/15 Torr, $n^{20}{}_D$ 1.4737, purity (G.C.) 100%; ^{1}H-NMR 1.45; 0.98 ppm; ^{13}C-NMR 27.87; 20.42; 16.59 ppm; exact mass calcd. 204.0859, found 204.0934.

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