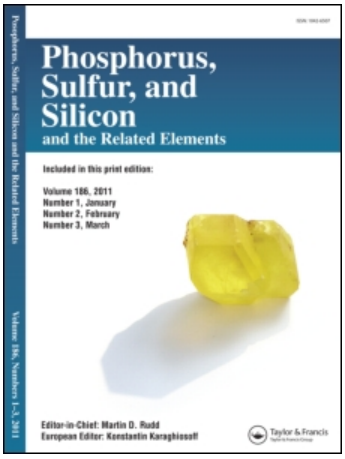


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

FISSION OF AS-AS BONDS IN ELEMENTAL ARSENIC BY ALKALI METALS IN LIQUID AMMONIA. A ROUTE TO MONOALKYL ARSINES

L. Brandsma[a]; O. Bjørlo[b]; A. C.H.T.M. van der kerk-van Hoof[a]; H. W. A. Biessels[a]; J. Schuring[a]; H. D. Verkruijsse[a]
[a] Faculty of Chemistry, Utrecht University, CH-Utrecht, The Netherlands [b] Trondheim College of Engineering, Trondheim, Norway

To cite this Article Brandsma, L. , Bjørlo, O. , Hoof, A. C.H.T.M. van der kerk-van , Biessels, H. W. A. , Schuring, J. and Verkruijsse, H. D.(2000) 'FISSION OF AS-AS BONDS IN ELEMENTAL ARSENIC BY ALKALI METALS IN LIQUID AMMONIA. A ROUTE TO MONOALKYL ARSINES', Phosphorus, Sulfur, and Silicon and the Related Elements, 166: 1, 261 — 264
To link to this Article: DOI: 10.1080/10426500008076547
URL: http://dx.doi.org/10.1080/10426500008076547

Phosphorus, Sulfur and Silicon, 2000, Vol. 166, pp. 261-264
Reprints available directly from the publisher
Photocopying permitted by license only

FISSION OF AS-AS BONDS IN ELEMENTAL ARSENIC BY ALKALI METALS IN LIQUID AMMONIA. A ROUTE TO MONOALKYL ARSINES

L. BRANDSMA[a*], O. BJØRLO[b], A.C.H.T.M. VAN DER KERK-VAN HOOF[a], H.W.A. BIESSELS[a], J. SCHURING[a] and H.D. VERKRUIJSSE[a]

[a]*Faculty of Chemistry, Utrecht University, Padualaan 8, 3584 CH-Utrecht, The Netherlands and* [b]*Trondheim College of Engineering, E.C. Dahls Gate 2, N-7004, Trondheim, Norway*

(Received July 11, 2000)

Addition of two mol equivalents of *t*-butyl alcohol to a mixture of powdered arsenic and three mol equivalents of lithium in liquid ammonia gives a suspension of lithium arsenide $LiAsH_2$. Subsequent addition of a large excess of *t*-butyl alcohol and *n*-octyl iodide at very low temperatures affords *n*-octyl arsine in ~65% yield.

Keywords: Arsines-acidity of; Alkali metal arsenides-alkylation of; Lithium tert., butoxide-solvation by tert. butyl alcohol; Lithium arsenide-monoalkylation of

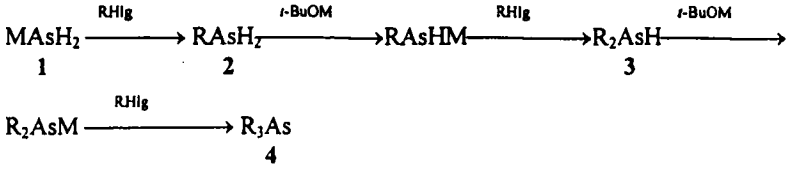
INTRODUCTION

In a previous communication[1] we reported that elemental arsenic can be successfully converted into alkali arsenide, $MAsH_2$, by *t*-butyl alcohol-assisted reaction with alkali metals in liquid ammonia:

$$As + 3\,M + 2\,t\text{-}BuOH \xrightarrow{\text{liq. ammonia}} MAsH_2 + 2\,t\text{-}BuOM\ (M = Li, Na, K)$$

* Corresponding Author.

Reaction of the resulting suspensions with primary alkyl halides did not afford the expected monoalkyl arsines **2** but mixtures of dialkyl arsines **3** and trialkyl arsines **4** were obtained as a result of alternating deprotonation and alkylation sequences:



We assume that the alkali *t*-butoxide formed in the reaction of arsenic with the alkali metal and *t*-butyl alcohol is strong enough to give rise to significant equilibrium concentrations of the arsenides RAsHM and R_2AsM.

RESULTS AND DISCUSSION

Addition of an excess of *t*-butyl alcohol was thought to reduce the basicity of *t*-butoxide so that deprotonation of **2** and further alkylation would be hindered. However, under these conditions also the volatile AsH_3 (b.p. $-62.4°$ C[2]) could be formed. Therefore, the excess of *t*-butyl alcohol and a sufficiently reactive alkyl halide should be added at temperatures below $-70°$ C.

Based on these considerations we used As, Li and t-BuOH in the molar ratio of 1:3:4 instead of 1:3:2. Subsequent alkylation, however, afforded predominantly dialkyl arsine, R2AsH. Apparently, stronger solvation of the t-butoxide was necessary, therefore we made an attempt with 6 equivalents of t-butyl alcohol, which gave a satisfactory result.

A 1-L round-bottomed, three-necked flask (vertical necks) was equipped with a gas inlet-thermometer combination, a mechanical stirrer (reaching nearly until the bottom of the flask) and a dropping funnel-outlet combination. The flask was charged with 450 ml of liquid ammonia (water content <0.1%) and nitrogen was slowly introduced (~ 200 ml/min). After cooling to $-45°$ C, 4.2 g (0.6 mol) of lithium, cut into pieces of 0.2 to 0.4 g, was

introduced. Lumps of arsenic were ground in a mortar to a dusty powder (15.3 g, 0.20 mol plus 0.3 g excess). The powder was cautiously introduced through a powder funnel into the flask. After stirring for half an hour a mixture of 30 g (~0.4 mol) of *t*-butyl alcohol and 30 ml of dry THF was added drop wise over 2 h with stirring at a moderate rate while maintaining the slow introduction of nitrogen and an internal temperature of ~-40°C. At the end of the addition the colour of the reaction mixture changed from deep blue to green or yellowish-green. The temperature was lowered to – 75°C (bath with liquid nitrogen, temporary increase of the flow of nitrogen) and 0.8 mol (~60 g) of *t*-butyl alcohol was added over a few min followed by 43 g (0.18 mol) of *n*-octyl iodide. The mixture was vigorously stirred and its temperature maintained between –65 and –70° C. After 15 min the temperature was allowed to rise to –40° C. After an additional period of 30 min 30 g of finely powdered ammonium chloride was introduced (the dropping funnel was replaced with a powder funnel and the flow rate of nitrogen increased to ~ 0.5 L/min) in small portions over 15 min, while maintaining the temperature of the reaction mixture at ~-40°C. The ammonia was then removed by placing the flask in a water bath at ~40°C and increasing the flow of nitrogen to ~ 1 L/min (the outlet being removed). If necessary, small amounts of diethyl ether or pentane were added to suppress foaming. When the flow of ammonia vapour had become weak, 250 ml of pentane and 300 ml of deaerated water were successively added with stirring. After dissolution of the salts, the layers were separated (the presence of some brown solid material may cause some problems during the separation) and the aqueous layer extracted once with 200 ml of pentane. The combined organic solutions were washed once with 500 ml of an aqueous solution of 50 g of ammonium chloride (deaerated !) in order to remove most of the *t*-butyl alcohol and subsequently dried on $MgSO_4$. The liquid remaining after removal of the volatile components in a water-aspirator vacuum was distilled through a 20-cm Vigreux column. *n*-Octyl arsine, b.p. ~60° C/0.5 mm Hg, was obtained as a colourless liquid in 65% yield. The purity (G.C.) was 94%. The expected parent peak was present in the mass spectrum. The ^1H NMR spectrum (Bruker AC-300, solvent $CDCl_3$) showed a triplet at 2.14 ppm and multiplets around 1.57, 1.25 and 0.86 ppm and the ^{13}C spectrum showed signals at 12.24, 14.07, 22.67, 29.14, 29.24, 31.33, 31.88 and 32.84 ppm.

Note: The product is extremely oxygen-sensitive. Contact with air immediately caused formation of a white solid insoluble in organic sol-

vents, but easily removable by rinsing with dilute aqueous alkali hydroxide. All operations during the synthesis were scrupulously carried out under inert gas.

References

1. L. Brandsma, O. Björlo, A.C.H.T.M. van der Kerk-van Hoof, Phosphorus, Sulfur and Silicon, **162, page? (2000)**.
2. W.C. Johnson and A. Pechukas, J. Amer. Chem. Soc., **59**, 2065 (1937).