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THE REACTION OF POTASSIUM DIHYDROGEN ARSENIDE WITH HALOBENZENES

HARNG-SHEN KUO AND WILLIAM L. JOLLY

The Inorganic Materials Research Division of the Lawrence Radiation Laboratory, and the Department of Chemistry, University of California, Berkeley, California 94720 (U.S.A.)

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SUMMARY

Potassium dihydrogen arsenide reacts with aryl halides at ambient temperature to give benzene, tetraphenyldiarsine and triphenylarsine. The yield of benzene ranged from 74% in the case of iodobenzene to 0% in the case of chlorobenzene. The normal coupling product, triphenylarsine, was obtained (in low yields) only from chlorobenzene and bromobenzene.

INTRODUCTION

Nucleophilic attack on the halogen atoms of organic halides constitutes a well-documented class of reactions. Evidence for such attack by various nucleophilic reagents, including the triphenylsilyl anion[1], germyl anions[2,3], and phosphines[4], has been cited. In this paper we report the results of a study of the reaction of diglyme solutions of potassium dihydrogen arsenide ($KAsH_2$) with iodo-, bromo- and chlorobenzene. Of particular interest, from a synthetic point of view, were the relative yields of benzene (from attack on halogen atoms) and phenylarsines (from coupling reactions).

EXPERIMENTAL

General

Arsine and arsine-d_3 were synthesized[5]; the other chemicals were commercially available. The infrared spectrum of the arsine-d_3 showed no trace of the As–H stretching band. Diglyme was distilled from potassium hydroxide and then vacuum-distilled from lithium aluminium hydride. The potassium dihydrogen arsenide solutions were prepared by quantitatively deprotonating arsine with a suspension of potassium hydroxide in diglyme, and the yellow $KAsH_2$ solution was filtered through a medium-porosity frit into the reaction vessel[6].

Reaction with bromobenzene

Bromobenzene (4.57 mmoles) was added to a solution of 4.57 mmoles of $KAsH_2$ in diglyme. The reaction mixture was held at room temperature for 12 h, during which time the color of the solution changed from yellow to blood-red. After removal of the volatile products, the blood-red moist solid remaining in the reaction vessel was heated *in vacuo* ($< 5 \times 10^{-2}$ mm) first at 150° (to obtain triphenylarsine and a trace of diphenylarsine) and then at 200° (to obtain tetraphenyldiarsine). Preliminary experiments showed that these same products could be separated from the moist red solid by extraction with benzene at room temperature. Triphenylarsine was identified by its proton magnetic resonance, mass and infrared spectra[7], and quantitatively converted to $(C_6H_5)_3As \cdot HgCl_2$[8], m.p. 245–247° (lit.[9] 247–248°). The crude tetraphenyldiarsine was recrystallized from ether, m.p. 129–130° (lit.[10] 128–130°). Confirmatory identification of the tetraphenyldiarsine was achieved by treatment with $HgCl_2$ in ethanol to form Hg[11] and by quantitative conversion to $(CH_3)_2(C_6H_5)_2AsI$ by treatment with CH_3I, m.p. 190° (lit.[12] 189°). No unreacted bromobenzene was found among the volatile products. The amount of diphenylarsine obtained was about 5 per cent of the triphenylarsine obtained, on the basis of the NMR spectrum of the mixture. Extraction of the nonvolatile residue with hot benzene yielded no further products.

Reaction with iodobenzene

Iodobenzene (5.09 mmoles) was added to 5.64 mmoles of $KAsH_2$ in diglyme solution. The results were similar to those of the bromobenzene reaction, except the solution turned from yellow to dark red immediately, and only tetraphenyldiarsine was found.

Reaction with chlorobenzene

Chlorobenzene (8.89 mmoles) was added to 9.92 mmoles of $KAsH_2$ in diglyme solution. The reaction procedure was the same as before, except one week at room temperature was required for the solution to become orange-red, and benzene was not found.

A similar reaction, between 9.07 mmoles of chlorobenzene and 9.14 mmoles of $KAsH_2$ in diglyme, was carried out at higher temperature (70–80°). Again, benzene was not found. In these experiments, unreacted chlorobenzene was found among the volatile products.

Deuterium experiments

A diglyme solution approximately 1 *M* in AsD_2^- was sealed in an NMR tube. The proton NMR spectrum did not show any AsH_2^- or $AsHD^-$ species after one week at room temperature, thus proving the absence of any proton exchange with the solvent.

A solution of 7.24 mmoles of $KAsD_2$ in diglyme was treated with 7.15 mmoles of bromobenzene. The benzene (2.32 mmoles) was shown by mass spectrometry to be essentially pure C_6H_5D. (The peak ratio for masses 79, 80 and 81 was 100/7.15/0.12, whereas the ratio for masses 78, 79 and 80 in ordinary benzene is 100/6.93/0.99.) The arsine (1.41 mmoles) was estimated to be at least 95% AsD_3 on the basis of its infrared spectrum. The small amount of evolved hydrogen was principally D_2.

DISCUSSION

The yields of the volatile products of the reactions of $KAsH_2$ with the halo-

TABLE 1

VOLATILE PRODUCTS OF THE REACTION OF KAsH$_2$ WITH C$_6$H$_5$X

X	Reaction time (h)	Reaction temp. (°C)	Yields, moles/mole of KAsH$_2$				
			AsH$_3$	H$_2$	C$_6$H$_6$	As(C$_6$H$_5$)$_3$	As$_2$(C$_6$H$_5$)$_4$
Cl	150	22	0.093	0.0028	0	0.018	0
	24	75	0.024	0.020	0	0.013	0
B	12	23	0.17	0.0060	0.35	0.022	0.057
I	2	22	0.17	0.012	0.74	0	0.035

benzenes are listed in Table 1.

Issleib and Kümmel[13] have shown that phenylarsine and diphenylarsine are stronger acids than arsine. Thus these substituted arsines would be expected to be deprotonated by the conjugate base of arsine (AsH_2^-) which was present in our reaction mixture. The normal coupling reaction between potassium dihydrogen arsenide and a halobenzene probably proceeds through an alternating sequence of substitution reactions and proton transfer reactions, as follows:

$$AsH_2^- + C_6H_5X \rightarrow C_6H_5AsH_2 + X^-$$
$$AsH_2^- + C_6H_5AsH_2 \rightarrow AsH_3 + C_6H_5AsH^-$$
$$C_6H_5AsH^- + C_6H_5X \rightarrow (C_6H_5)_2AsH + X^-$$
$$AsH_2^- + (C_6H_5)_2AsH \rightarrow AsH_3 + (C_6H_5)_2As^-$$
$$(C_6H_5)_2As^- + C_6H_5X \rightarrow (C_6H_5)_3As + X^-$$

The overall reaction is as follows:

$$3\,AsH_2^- + 3\,C_6H_5X \rightarrow 2\,AsH_3 + (C_6H_5)_3As$$

This mechanism explains why no phenylarsine and very little diphenylarsine is formed in such reactions, and it accounts for the formation of the triphenylarsine and at least part of the arsine.

Attack of the AsH_2^- ion on the halogen atom of a halobenzene molecule yields benzene, presumably via the formation of the phenyl anion and the haloarsine:

$$AsH_2^- + C_6H_5X \rightarrow AsH_2X + C_6H_5^-$$
$$C_6H_5^- + AsH_2X \rightarrow C_6H_6 + 1/x(AsH)_x + X^-$$

The "$(AsH)_x$" would be expected to decompose to arsine, hydrogen, and a polymeric product of approximate stoichiometry $AsH_{0.5}$.[14] This decomposition probably accounts for the small amounts of hydrogen formed in the reactions. Similar halogen-atom attack by the $(C_6H_5)_2As^-$ ion can account for the formation of tetraphenyldiarsine:

$$(C_6H_5)_2As^- + C_6H_5X \rightarrow (C_6H_5)_2AsX + C_6H_5^-$$
$$(C_6H_5)_2AsX + (C_6H_5)_2As^- \rightarrow As_2(C_6H_5)_4 + X^-$$
$$C_6H_5^- + AsH_3 \rightarrow AsH_2^- + C_6H_6$$

These mechanisms account for the deuterium experiments, which showed that the hydrogen atom which replaces the halogen atom of the halobenzene originated in the AsH_2^- ion.

Attack on the halogen atom (and the yield of benzene) would be expected to be favored by increasing electropositive character and polarizability of the halogen atom. Thus the best yield of benzene is obtained with iodobenzene, and the poorest yield (none) is obtained with chlorobenzene. In the case of iodobenzene, the benzene-producing reactions are so fast that none of the normal coupling product (triphenylarsine) is obtained. In the case of chlorobenzene, the normal coupling reaction is so slow that a very poor yield of triphenylarsine is obtained. Raising the temperature does not improve the yield because of decomposition of the $KAsH_2$.

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