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A NEW SYNTHESIS OF DI- AND TRI-TERTIARY ARSINES

ROBERT D. FELTHAM*, A. KASENALLY AND R. S. NYHOLM

Department of Chemistry, The University of Arizona, Tucson, Ariz. (U.S.A.)
and
The William Ramsey and Ralph Forster Laboratories, University College London (Great Britain)

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Polydentate compounds of the general type $(R_2As)_nR'$ have been of interest to inorganic chemists since the compound *o*-phenylenebis(dimethylarsine) was prepared and its palladium derivatives characterized by Chatt and Mann[1]. Subsequently, a variety of polydentate arsines has been prepared and their metal complexes characterized (see *e.g.* refs. 2 and 3). One serious limitation to further progress in this area has been the lack of suitable methods of synthesis of the arsine ligands. For example, the method used by Chatt and Mann for the synthesis of *o*-phenylenebis(dimethylarsine) involves four steps with an overall yield of only 20%. It was therefore desirable to find more direct and general methods for the preparation of compounds containing $-AsR_2$ groups. A new general method for the preparation of polytertiary arsine compounds is the subject of this communication.

EXPERIMENTAL

Because of the toxic nature of the compounds concerned, all operations were carried out in an efficient hood. Cacodylic acid, *o*-dichlorobenzene and tetrahydrofuran were obtained from British Drug Houses or Fisher Scientific Co., and 1,1′,1″-tris(hydroxymethyl)ethane was obtained from Aldrich Chemical Co. The solvents were dried over 1/16 in. pellets of "Molecular Sieve" from the Linde Co., and the other reagents were used without further purification. All of the compounds are sensitive to oxygen and water, and therefore the reactions were carried out under nitrogen.

$(CH_3)_2AsI$

This compound was prepared using the method of Burrows and Turner[4] with only minor modifications. The procedure consists of dissolving dimethylarsinic acid in water along with potassium iodide and adding hydrochloric acid and sulphur dioxide simultaneously. It was found that the hydrochloric acid should be added to the aqueous solution as rapidly as possible (5 min). Slow addition of acid favors the formation of metallic arsenic and lower yields of the compound $(CH_3)_2AsI$. After completion of the reaction, the lower layer of dark yellow to red product was separated,

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dried over Molecular Sieve and stored in flasks of low actinide glass. The compound was used directly without further purification. The yields were 90–95% based on the cacodylic acid used.

$(CH_3)_2AsH$

This compound was prepared by reducing dimethylarsinic acid with zinc/hydrochloric acid[5]. The flask containing the reducing agent was maintained at 40° so that the dimethylarsine distilled as it was formed. The dimethylarsine was passed through a trap containing Molecular Sieve and condensed using a Dry Ice/acetone bath. The yields were 90–95% based on cacodylic acid, b.p. 35–37° (760 mm).

$CH_3C(CH_2Br)_3$

This compound was prepared by treating 1,1′,1″-tris(hydroxymethyl)ethane with phosphorus tribromide under conditions identical with those described for the preparation of pentaerythritylbromide[6]. The yield was 54.5% based on the alcohol, b.p. 119–120° (17 mm); n_D^{20} 1.5623; NMR singlets at τ 6.49 ppm and 8.70 ppm with an area ratio of 2.0:1.0.

o-$C_6H_4[As(CH_3)_2]_2$

Method I. After several preliminary experiments using lithium sodium and potassium metals, sodium was selected because it was found to be more reactive than lithium, and is more easily handled in this reaction than potassium. Two liters of tetrahydrofuran and 115 g of sodium in the form of 1/4 to 1/8 in. pellets (5.0 moles) were placed in a 4-l three-necked round-bottomed flask equipped with a nitrogen inlet and outlet, mechanical stirrer (not a magnetic stirrer), and 500-ml dropping funnel. It was found that smaller pellets of sodium were unnecessary since the sodium fuses into a porous ball during the course of the reaction. The whole flask was placed in a bath of ligroin. The addition of 510 g (2.2 moles) of the iodide $(CH_3)_2AsI$ was begun cautiously at a slow rate (dropwise). The initial stage of this reaction is important since if it is not initiated correctly, it will "take off" later in a manner similar to that observed in Grignard reactions. The reaction has begun when the solution turns bright yellow, and solid sodium iodide appears. The ligroin bath was then cooled to 0° by the addition of Dry Ice, and the addition of dimethyliodoarsine was completed over a period of 1–2 h. Stirring was continued for another half hour, and at the end of this time, 161.7 g (1.10 moles) of o-dichlorobenzene was slowly added with cooling. The resultant mixture was allowed to stand under nitrogen for 16 h, and the tetrahydrofuran was removed by distillation at atmospheric pressure using a steam bath. The resultant white residue was cooled and 2 l of water were added to dissolve the sodium salts which had formed (*caution*! sodium metal is always present in these residues). The lower layer (a total of 260 g) was transferred under nitrogen into a 500-ml two-necked flask equipped with a nitrogen inlet and outlet, and a 47-cm Vigreaux column. After removing the residual tetrahydrofuran and water (10 mm), the crude product was vacuum-distilled, giving 93.7 g (44.5% based on dimethyliodoarsine) of o-phenylenebis(dimethylarsine), b.p. 100–101° (1.0 mm); n_D^{25} 1.6156 (lit. n_D^{20} 1.6204). (Found C, 41.65; H, 5.65. $C_{10}H_{16}As_2$ calcd.: C, 41.99; H, 5.64%.)

A methiodide was prepared by reacting 1 ml of the distillate with 15 ml of

CH_3I. Recrystallization from acetone gave colorless plates, m.p. 226–230° (lit. 228–230°). (Found: C, 31.8; H, 4.57. $C_{11}H_{19}As_2I$ calcd.: C, 30.87; H, 4.47%.)

Method II. Twenty seven g of sodium sand was prepared in 300 ml of toluene[7], the toluene was poured off and replaced by 300 ml of tetrahydrofuran, and the flask was equipped as described above. A total of 95.4 g of dimethylarsine was slowly distilled through a trap containing Molecular Sieve into the tetrahydrofuran/sodium sand slurry maintained at a temperature of −10 to −20°. The solution was allowed to warm to room temperature after the final dimethylarsine had been added and then the rest of the preparation was carried out as described above. The yield of *o*-phenylenebis(dimethylarsine) was 48% based on the dimethylarsine added, and has been characterized by preparing various transition metal chelates[8].

$CH_3C[CH_2As(CH_3)_2]_3$

The preparation of this compound was carried out as described above in method I and method II except $CH_3C(CH_2Br)_3$ was used in place of *o*-dichlorobenzene. The water-insoluble layer was vacuum distilled to give 1,1′,1″-tris(dimethylarsinomethyl)ethane, b.p. 110–111° (0.7 mm); n_D^{20} 1.5623; d_{20} 1.3575; NMR: three singlets at τ 8.29, 8.94 and 9.05 ppm with an area ratio of 2.0 : 1.07 : 6.0. The yields of 1,1′,1″-tris(dimethylarsinomethyl)ethane ranged from 47–55% using either method I or II based on the arsine used. (Found: C, 20.71; H, 4.74. $C_{11}H_{27}As_3$ calcd.: C, 20.74; H, 4.44%.)

RESULTS AND DISCUSSION

The reaction of sodium with iododimethylarsine to form dimethylarsinosodium, $(CH_3)_2AsNa$, is not unexpected since it has long been known that the analogous reaction with zinc metal leads to the formation of tetramethyldiarsine[5], and that this in turn can be cleaved with sodium to give the derivative $(CH_3)_2AsNa$. Since under the conditions described above the yield of aliphatic and aromatic arsines is only about 50%, it appeared that only 50–60% of the theoretical amount of $(CH_3)_2AsNa$ was being produced from the reaction of sodium with iododimethylarsine. Reaction (1) could be expected to be a major side reaction when an appreciable concentration of dimethylarsinosodium is present, and therefore the sodium salt was prepared using dimethylarsine. When dimethylarsine is used, no tetramethyldiarsine can be formed. Essentially identical yields of *o*-phenylenebis(dimethylarsine) and 1,1,1-tris(dimethylarsinomethyl)ethane were obtained when dimethylarsine was used to prepare the sodium salt. Unfortunately, it has thus far proved impossible to analyze the products from the reaction between sodium and dimethylarsine in an unambiguous way, but the low yields still appear to be associated with the formation of dimethylarsinosodium, followed by high yields from reaction (2) or (3).

$$(CH_3)_2AsI + (CH_3)_2AsNa \rightarrow [(CH_3)_2As]_2 \qquad (1)$$

$$2\,(CH_3)_2AsNa + o\text{-}C_6H_4Cl_2 \rightarrow o\text{-}C_6H_4[As(CH_3)_2]_2 + 2\,NaCl \qquad (2)$$

$$2\,(CH_3)_2AsNa + CH_3C(CH_2Br)_3 \rightarrow CH_3C[CH_2As(CH_3)_2]_3 + 3\,NaBr \qquad (3)$$

The reaction of dimethylarsinosodium with *o*-dichlorobenzene is very energetic, requiring cooling to prevent undesirable increases in the reaction temperature.

In view of the usual inertness of unsubstituted aromatic halides to substitution by good nucleophiles[9,10,11] this reaction is most unusual, and further work is in progress to define the course of these reactions more clearly. The aliphatic halides and the aromatic halides give the same overall yield, thus the presence of benzyne as an important intermediate in the reaction of dimethylarsinosodium with *o*-dichlorobenzene is highly unlikely. Further, if benzyne were an intermediate some chloro substituted *o*-phenylenebis(dimethylarsine) would be expected. Analysis of *o*-phenylenebis(dimethylarsine) for chloride showed that there was less than 0.1 % chloride present. Therefore, the reaction probably proceeds by nucleophilic substitution of the halogen by the anion $(CH_3)_2As^-$.

The reaction of dimethylarsinosodium with *o*-dichlorobenzene undoubtedly proceeds stepwise, so careful observations of column temperatures were made during distillation, and the crude products were analyzed by gas–liquid chromatography for (*o*-chlorophenyl)dimethylarsine but no trace of it was found.

The reaction of dimethylarsinosodium with the bromide $CH_3C(CH_2Br)_3$ proceeded smoothly, but again to give only a 50% yield. Previous studies of reactions of this type[12] show that the reactions between alkali metal derivatives of secondary arsines and alkyl halides give good yields of tertiary arsines, which again indicates that only 50% yields of the compound $(CH_3)_2AsNa$ are obtained in the first step.

SUMMARY

A new synthesis of di- and tri-tertiary arsines is described. This method involves the reaction of dimethylarsinosodium with organic halides, and appears to be of general applicability. The anion $(CH_3)_2As$ appears to be an extremely reactive nucleophile, giving exothermic reactions with aryl halides as inert as *o*-dichlorobenzene.

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