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INTERACTION OF ARYLTRIMETHYLSTANNANES WITH CYANOGEN CHLORIDE AND BROMIDE. A ROUTE TO ARYL CYANIDES

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SUMMARY

Phenyltrimethylstannane has been found to react with cyanogen chloride in methylene chloride in the presence of aluminium chloride to give benzonitrile in 60% yield; *o*-, *m*-, and *p*-tolyltrimethylstannane similarly give *o*-, *m*-, and *p*-tolunitrile, respectively. With cyanogen bromide the aryl bromides are formed.

Phenyltrimethylsilane does not react with cyanogen chloride in the presence of aluminium chloride, but gives bromobenzene when treated with cyanogen bromide in methylene chloride in the presence of aluminium chloride.

INTRODUCTION

Cleavages of aryl–MR_3 bonds, where M = Si, Ge, Sn or Pb, by electrophilic reagents can provide useful methods of introducing functional groups into aromatic rings at specific, predetermined positions. For example, we recently described the preparation of isomerically-pure nitroso compounds, XC_6H_4NO, by treatment of the corresponding $XC_6H_4SnMe_3$ compounds with nitrosyl chloride[1], and earlier papers were concerned with the use of cleavages of $XC_6H_4MR_3$ compounds, with M = Si and/or Sn, to give the XC_6H_4Y compounds with Y = SO_3H[2], NO_2[3], RCO[4], RSO_2[5]. The preparation of aryl iodides by use of iodine monochloride in this type of reaction has also recently been demonstrated[6]. In seeking an analogous route to XC_6H_4CN compounds, we briefly examined the reactions of $XC_6H_4MMe_3$ compounds having M = Si and Sn with cyanogen chloride and cyanogen bromide. The study was not as complete as we would wish, but since there is no prospect of its extension in the near future we report below the limited results obtained*.

RESULTS AND DISCUSSION

Phenyltrimethylstannane gave benzonitrile in 60% yield on treatment with cyanogen chloride in methylene chloride in the presence of aluminium chloride. The *o*-, *m*-, and *p*-tolyltrimethylstannanes gave the corresponding *o*-, *m*-, and *p*-tolunitriles in 30, 30 and 60% yield, respectively; some aryltrimethylstannane was

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* A preliminary report has previously appeared[7].

recovered in each case, and no attempt was made to find conditions which would maximize the yield. The reaction offers a novel route to aryl cyanides. Phenyltrimethylsilane did not undergo significant reaction under the conditions used; aryltrimethylsilanes involving strongly activated aromatic rings could be expected to enter the reaction, however.

The reactions with cyanogen bromide in presence of aluminium chloride took a different course. Phenyltrimethylstannane gave bromobenzene in 60% yield in a reaction in absence of solvent, while the tolyltrimethylstannanes gave 74, 60, and 30% yields of *m*-, *p*-, and *o*-bromotoluene, respectively, in reactions in carbon disulphide. Phenyltrimethylsilane entered into this reaction in methylene chloride, to give bromobenzene, but less readily than its tin analogue, as would be expected.

The contrasting behaviour of cyanogen bromide and cyanogen chloride has been observed previously in reactions with Grignard reagents; thus some aryl- and alkynyl-magnesium halides, RMgX, are known to react with cyanogen chloride to give the nitriles, RCN, but with cyanogen chloride to give the bromides, RBr[8,9].

EXPERIMENTAL

Interaction of aryltrimethylstannanes and cyanogen chloride

(i) Cyanogen chloride (3.0 g, 0.049 mole) was carefully added with stirring and exclusion of moisture to a cooled solution of phenyltrimethylstannane (9.6 g, 0.040 mole) and finely-powdered anhydrous aluminium chloride (5.3 g, 0.040 mole) in anhydrous methylene chloride kept at 0°. When the mixture was gently warmed to 35°, reaction set in and heat was developed. The mixture was subsequently kept at 35° for 2 h, then cooled and poured onto ice. The organic layer was separated, washed with dilute alkali followed by water, dried (Na_2SO_4), and fractionally distilled to give benzonitrile (2.4 g, 60%), b.p. 191°, which had an IR spectrum identical with that of an authentic sample.

(ii) The three tolyltrimethylstannanes analogously gave *o*- (30%), b.p. 204°, ν(C≡N) 2230 cm^{-1} [lit.[10,11], b.p. 205°, ν(C≡N), 2230 cm^{-1}], *m*- (30%), b.p. 210°, ν(C≡N) 2240 cm^{-1} [lit.[12], b.p. 210–212°], and *p*-tolunitrile (60%), b.p. 216°, m.p. ca. 26–28°, ν(C≡N) 2230 cm^{-1} [lit.[10,13], b.p. 218°, m.p. 29°, ν(C≡N), 2230 cm^{-1}]. Some unchanged tolyltrimethylstannane was recovered in each case.

Treatment of phenyltrimethylsilane with cyanogen chloride

Under conditions identical with those used for the tin analogue, phenyltrimethylsilane gave no benzonitrile, and ca. 90% of the phenyltrimethylsilane was recovered.

Interaction of aryltrimethylstannanes and cyanogen bromide

(i) A vigorous reaction began when cyanogen bromide (2.5 g, 0.024 mole) was added carefully with exclusion of moisture to phenyltrimethylstannane (5.0 g, 0.021 mole) and finely-powdered aluminium chloride (3.5 g, 0.026 mole). The mixture was subsequently stirred for 1 h at room temperature then added to ice. Ether extraction was followed by separation of the extract, which was washed twice with aqueous sodium hydroxide to destroy residual cyanogen bromide, and then with water. The ethereal solution was dried (Na_2SO_4) and fractionated, to give bromobenzene (2.0 g, 60%), b.p. 155°; the IR spectrum was identical with that of an authentic sample.

(ii) Unchanged phenyltrimethylstannane and cyanogen bromide were recovered in high yield by distillation after 10 h refluxing in ether in absence of aluminium chloride, and no bromobenzene was isolated.

(iii) To *m*-tolyltrimethylstannane (10.0 g, 0.039 mole) in carbon disulphide (10 ml) was added finely divided aluminium chloride (5.8 g, 0.043 mole), followed by cyanogen bromide (4.6 g, 0.043 mole) in carbon disulphide (20 ml); the mixture boiled under its own heat during the addition of the cyanogen bromide solution. The mixture was refluxed for 1 h, then worked up as in (i) to give *m*-bromotoluene (5.0 g, 74%), b.p. 184°, having an IR spectrum identical with that of an authentic sample.

Analogously *o*- and *p*-tolyltrimethylstannane gave *o*- (30%) and *p*-bromotoluene (60%), respectively.

Interaction of phenyltrimethylsilane and cyanogen bromide

Cyanogen bromide (2.2 g, 0.020 mole) was added with stirring and exclusion of moisture to a stirred solution of phenyltrimethylsilane (3.0 g, 0.020 mole) and aluminium chloride (2.7 g, 0.020 mole) in methylene chloride (10 ml). The mixture was kept at 40° for 2 h then added to ice. Working up in the usual way gave unchanged phenyltrimethylsilane (1.0 g, 33%) and bromobenzene (1.5 g, 48%), b.p. 155°.

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