

CCCXVII.—*The Interaction between Alkyl Grignard Reagents and Arsenic Trichloride.*

By WILFRED JAMES CECIL DYKE and WILLIAM JACOB JONES.

IN the present investigation it has been found that the chief product of the interaction between an alkyl Grignard reagent and arsenic trichloride is the trialkylarsine. Some arsenic is always liberated; it forms a finely divided, brown powder, and appears to be produced by the reducing action of the free arsine, which is present in the reaction mixture, on the added arsenic trichloride. Paraffin, formed during the preparation of the Grignard solution by the

synthetic action of the magnesium on the alkyl bromide, can be isolated by shaking the pre-arsine fraction in the final distillation with concentrated sulphuric acid.

Trialkylarsines are less readily oxidised than the corresponding stibines. They combine immediately, however, with bromine, and with iodine, and their avidity for alkyl halides is much greater than that of the stibines. With chlorine, trimethylarsine immediately bursts into flame. Reduction to finely divided, brown arsenic occurs when a tertiary arsine is slightly warmed with arsenic trichloride.

Gryszkiewicz-Trochimowski, Zambrzycki, and Sikorski (*Rocz. Chem.*, 1926, **6**, 794; 1927, **7**, 54; 1928, **8**, 250; *Bull. Soc. chim.*, 1927, **41**, 1570) have prepared the tertiary *n*-alkylarsines from methyl to octyl by treating Grignard reagents with arsenious oxide, and have recorded measurements of their refractive indices. The atomic refractivity of arsenic in the new triisoalkylarsines now described, calculated by deducting the atomic refractivities of the carbon and the hydrogen (*Eisenlohr, Z. physikal. Chem.*, 1910, **75**, 585) from the values of the molecular refractivities, [R_L] (see Experimental), is given in the following table.

Arsine.	Atomic Refractivity of Arsenic.		
	F.	D.	C.
<i>Triisobutyl</i>	12.31	11.94	11.80
<i>Tri-di-amy</i> l	11.83	11.46	11.32
<i>Triisoamyl</i>	12.34	11.96	11.79
<i>Trisohexyl</i>	12.35	12.00	11.86

For comparison, it may be added that the value given by Gryszkiewicz-Trochimowski and Sikorski for the atomic refractivity of arsenic for D light is 11.46 in triethylarsine, and 10.97 in tri-*n*-propylarsine.

EXPERIMENTAL.

The apparatus and procedure employed in the investigation of the interactions between Grignard reagents and antimony trichloride (Dyke, Davies, and Jones, this vol., p. 465) were adopted in the present work, the arsine being finally isolated by fractional distillation under reduced pressure.

For the analyses, as in the case of the stibines, tared, constricted glass tubes were quarter-filled with 0.1—0.2 g. of the arsine inside a chamber filled with carbon dioxide (Dyke and Jones, this vol., p. 1923), and were then quickly sealed off. In the determinations of carbon and hydrogen, a mixture of powdered lead chromate and copper oxide was used to surround the tube, whose seal had been broken immediately before introduction. Arsenic was determined by the method of Ewins (*J.*, 1916, **109**, 1356).

A mixture of diethyl ether and trimethylarsine was obtained by Hibbert (*Ber.*, 1906, **39**, 160) by distilling in carbon dioxide the product obtained on using approximately equivalent weights of magnesium, methyl iodide and arsenic tribromide. Owing to the closeness of the boiling points of the ether and trimethylarsine, 34.6° and 52°/760 mm. respectively, their separation by distillation is not convenient, and, therefore, in investigating the interaction between magnesium methyl iodide and arsenic trichloride we have chosen di-*n*-amyl ether as medium. The use of a high-boiling ether permits of easy isolation of the arsine through fractional distillation, and affords a convenient method of preparation, alternative to that recommended by Renshaw and Holm (*J. Amer. Chem. Soc.*, 1920, **42**, 1468), *viz.*, the action of arsenic trichloride on zinc methyl in xylene. The medium for the preparation of the Grignard reagent was obtained as follows. A mixture of 600 c.c. of *n*-amyl alcohol and 100 c.c. of 96% sulphuric acid was kept gently boiling in a distillation flask until the temperature of the liquid attained 170°. The heating lasted about 7 hours, and from the distillate consisting of a mixture of amylene, alcohol, ether and water, the upper layer was separated. The mixture in the flask was then steam-distilled, and the upper layer of the distillate was separated and added to that obtained from the distillate collected during the heating. The combined ethereal layers were washed with sodium carbonate solution, dried over calcium chloride, and fractionally distilled, the amylene, b. p. 40°, and alcohol, b. p. 138°, being rejected, and the distillate between 180° and 192° being collected. This was then refluxed for 3 hours with metallic sodium, filtered, allowed to stand over phosphoric oxide, decanted, and freshly distilled for use. The yield was 145 c.c.

A solution of magnesium methyl iodide was prepared by dropping 31 c.c. of methyl iodide in 70 c.c. of *i-n*-amyl ether on 12.1 g. of magnesium turnings immersed in 70 c.c. of the ether, to which a granule of iodine had been added. Dissolution of the magnesium began early, and the preparation of the Grignard reagent was complete in 3 hours, the reaction mixture being warmed to 40—50° towards the end. Then 13 c.c. of arsenic trichloride in 100 c.c. of *m*-xylene were added drop by drop during 2 hours. After the addition was complete, the stirring of the mixture was continued for 1 hour. The magnesium salt-complex was decomposed with a solution of 60 g. of ammonium chloride in 300 c.c. of water. Throughout all the preceding operations pure, dry hydrogen was passed through the reaction bottle. The ethereal layer was now removed in an atmosphere of carbon dioxide, dried, and fractionally distilled in a slow stream of carbon dioxide through an 8-pear column, the fraction 49—57° on being redistilled yielding 4.2 g. of trimethyl-

arsine, b. p. 51—53°. It may be noted that di-*n*-amyl ether has not hitherto been used as a medium for the preparation of Grignard reagents.

Auger and Billy (*Compt. rend.*, 1904, **139**, 597), owing apparently to the conditions of their experiment, did not obtain triethylarsine on treating the Grignard reagent with arsenic trichloride, but in the present work, 9 g. of purified triethylarsine were obtained by allowing 13.8 c.c. of arsenic trichloride in 100 c.c. of diethyl ether to react with the reagent prepared from 12.1 g. of magnesium, 55 g. of ethyl bromide, and 300 c.c. of diethyl ether, treating the mixture by the method of Dyke, Davies, and Jones (*loc. cit.*), and distilling the arsine, b. p. 138—139°/760 mm., in a stream of carbon dioxide. There was no evidence of the formation of any arsenic compound, other than the tertiary arsine, in this interaction.

Tri-*n*-butylarsine was prepared by the addition of the equivalent of arsenic trichloride in diethyl ether to the Grignard reagent prepared from 69 g. of *n*-butyl bromide. The yield of arsine, b. p. 150°/41 mm., was 10 g., and 5 g. of *n*-octane, b. p. 125°/760 mm., were obtained.

The preparation of *triisobutylarsine* (Found: C, 58.5; H, 11.5; As, 29.9. C₁₂H₂₇As requires C, 58.5; H, 11.1; As, 30.4%) was effected by adding arsenic trichloride to the Grignard reagent obtained from 69 g. of *isobutyl* bromide; yield of arsine, 9 g.; b. p. 119°/31 mm.; d_4^{25} 0.9590; n_D^{25} 1.4704; n_D^{25} 1.4627; n_C^{25} 1.4595; $[R_L]_F$ 71.67; $[R_L]_D$ 70.66; $[R_L]_C$ 70.24. In the preparation, 3 g. of β -dimethylhexane, b. p. 110°/765 mm., were obtained.

No tertiary arsine was obtained from the products of reaction of arsenic trichloride with magnesium *tert.*-butyl chloride.

Yields of 12 g. of tri-*n*-amylarsine, b. p. 179—180°/31 mm., and of 10 g. of *n*-decane, b. p. 169°/760 mm., were obtained when 13.8 c.c. of arsenic trichloride, 61 c.c. of *n*-amyl bromide, and 12.1 g. of magnesium were used.

Tri-dl- β -methylbutylarsine (*tri-dl-amylarsine*) (Found: C, 62.0; H, 11.6; As, 26.1. C₁₅H₃₃As requires C, 62.4; H, 11.5; As, 26.0%), b. p. 160°/28 mm., 149°/20 mm.; d_4^{25} 0.9563; n_D^{25} 1.4772; n_D^{25} 1.4696; n_C^{25} 1.4665; $[R_L]_F$ 85.19; $[R_L]_D$ 84.03; $[R_L]_C$ 83.55, was prepared by the interaction between arsenic trichloride and magnesium *dl*- β -methylbutyl bromide made from 76 g. of the alkyl bromide. Yield, 7 g. The first runnings furnished 10 g. of γ -dimethyloctane, b. p. 160°/760 mm.

Tri- γ -methylbutylarsine (*triisoamylarsine*) (Found: C, 62.2; H, 11.6; As, 25.9. C₁₅H₃₃As requires C, 62.4; H, 11.5; As, 26.0%), b. p. 167—168°/28 mm.; d_4^{25} 0.9504; n_D^{25} 1.4771; n_D^{25} 1.4694; n_C^{25} 1.4662; $[R_L]_F$ 85.71; $[R_L]_D$ 84.52; $[R_L]_C$ 84.02, was obtained from the

Grignard reagent made from 76 g. of *iso*amyl bromide (yield, 10 g.). The synthetic action of the magnesium gave 9 g. of $\beta\gamma$ -dimethyloctane, b. p. $160^\circ/760$ mm.

The interaction between the arsenic halide and the magnesium δ -methylamyl bromide made from 83 g. of the alkyl bromide gave 10 g. of *tri- δ -methylamylarsine* (*triisohexylarsine*) [Found : C, 65.0; H, 12.0; As, 22.0. $(C_6H_{13})_3As$ requires C, 65.4; H, 11.9; As, 22.7%], b. p. 158— $160^\circ/5$ mm.; d_4^{25} 0.9309; n_D^{25} 1.4741; n_D^{25} 1.4669; n_C^{25} 1.4639; $[R_L]_F$ 99.72; $[R_L]_D$ 98.42; $[R_L]_C$ 97.88. The first runnings furnished 5 g. of $\beta\iota$ -dimethyldecane, b. p. *ca.* $78^\circ/7$ mm.

Derivatives of the trialkylarsines are being investigated.

THE TATEM LABORATORIES, UNIVERSITY COLLEGE,

CARDIFF.

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