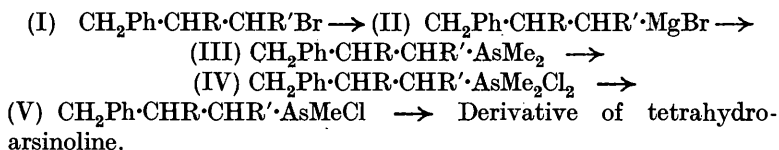


LXX.— $\gamma$ -Phenyl- $\alpha$ -methylpropyldimethylarsine,  $\beta$ -Benzylbutyldimethylarsine, and Some Related Compounds.

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BEFORE the appearance of the paper by Mills, Parkin, and Ward (J., 1927, 2613), we were attempting to prepare certain derivatives of dihydroarsindole and of tetrahydroarsinoline in which *cis-trans* isomerism should be exhibited. For one reason or another, no suitable ring arsines were obtained, but the results now recorded may be of value to future workers.

We have endeavoured to carry out a number of syntheses of the type :



$\beta$ -Benzylbutyl bromide (I; R = Et, R' = H) readily formed a Grignard reagent, but this reacted with dimethyliodoarsine to give only a poor yield of  $\beta$ -benzylbutyldimethylarsine (as III).

Neither  $\alpha\gamma$ -diphenylpropyl bromide (I; R = H, R' = Ph) nor  $\gamma$ -phenyl- $\alpha$ -m-chlorophenylpropyl bromide (I; R = H, R' = *m*-C<sub>6</sub>H<sub>4</sub>Cl) could be caused to combine with magnesium. On the other hand,  $\gamma$ -bromobutylbenzene readily formed a Grignard reagent, which reacted with dimethyliodoarsine to give  $\gamma$ -phenyl- $\alpha$ -methylpropyldimethylarsine, CH<sub>2</sub>Ph·CH<sub>2</sub>·CHMe·AsMe<sub>2</sub>. The dichloride (as IV) of this substance, however, underwent the expected loss of methyl chloride (on heating) only to the extent of a few units %, the major portion decomposing to give  $\gamma$ -chlorobutylbenzene and dimethylchloroarsine.

## EXPERIMENTAL.

$\beta$ -Benzylbutyl bromide, b. p. 135°/20 mm. (yield, 73%) (Found : Br, 34.9. C<sub>11</sub>H<sub>15</sub>Br requires Br, 35.2%), was prepared from  $\beta$ -benzylbutyl alcohol by means of phosphorus tribromide, the alcohol (b. p. 128—132°/11 mm.) being obtained in 73% yield by reducing ethyl  $\alpha$ -benzylbutyrate (b. p. 133—136°/15 mm.; 145—150°/20 mm.; 155—160°/30 mm.) with sodium and absolute alcohol. The most convenient synthesis of the ester proved to be the following : Benzylidenemalonic acid was prepared (43% yield) and reduced (yield, almost quantitative) by the methods of Claisen and

Crismer (*Annalen*, 1883, **218**, 135). Esterification of the benzylmalonic acid with alcohol and concentrated sulphuric acid proceeded to the extent of 75%, and the resulting ester (b. p. 170°/13 mm.) gave rise by normal procedure to a 90% yield of ethyl benzylethylmalonate. This was converted by Mohr's method (*J. pr. Chem.*, 1905, **71**, 331) into  $\alpha$ -benzylbutyric acid, b. p. 175—177°/20 mm. (yield, 77%).

*$\beta$ -Benzylbutyldimethylarsine.*—A solution of  $\beta$ -benzylbutyl bromide in three times its weight of ether was added gradually to slightly less than one atomic proportion of magnesium turnings, covered with ether, initial interaction being promoted by the use of iodine. Dimethyliodoarsine (1 mol.), dissolved in twice its volume of benzene, was slowly added to the formed Grignard reagent and the whole was gently boiled for an hour. Water and dilute hydrochloric acid were then added and the ether-benzene layer was worked up in the usual manner. The arsine, distilled in a current of hydrogen, was a colourless, strongly smelling oil, b. p. 150°/20 mm. (yield, 30%).

*$\alpha\gamma$ -Diphenylpropyl bromide;* b. p. 185—190°/30 mm. (Found: Br, 29.0.  $C_{15}H_{15}Br$  requires Br, 29.1%), was prepared by the action of phosphorus tribromide on the corresponding alcohol, which was obtained (80 g.) from benzaldehyde and the Grignard reagent from 100 g. of  $\beta$ -phenylethyl bromide.

*$\gamma$ -Bromobutylbenzene.*— $\beta$ -Phenylethyl bromide (170 g.) was converted into a Grignard reagent, and the latter was treated with 120% of the calculated quantity of acetaldehyde, dissolved in ether. An 85% yield of  $\beta$ -phenylethylmethylcarbinol, b. p. 124—126°/15 mm., or 128—130°/20 mm., was obtained, together with a small quantity of  $\alpha\delta$ -diphenylbutane. From 80 g. of the carbinol, by means of phosphorus tribromide, 90 g. of  *$\gamma$ -bromobutylbenzene*, b. p. 118—119°/14 mm., 129—130°/20 mm., or 137—138°/34 mm., were obtained (Found: Br, 36.9.  $C_{10}H_{13}Br$  requires Br, 37.5%).

*$\gamma$ -Phenyl- $\alpha$ -methylpropyldimethylarsine* was obtained in 56% yield from the interaction of dimethyliodoarsine and a Grignard reagent from  *$\gamma$ -bromobutylbenzene*. It is a colourless, highly refractive oil, b. p. 143—145°/20 mm., or 163°/50 mm. The *methiodide* was readily produced, and formed globular crystals, m. p. 156° (softening at 153°) (Found: I, 33.3.  $C_{13}H_{22}IA_s$  requires I, 33.5%).

*$\gamma$ -Phenyl- $\alpha$ -m-chlorophenylpropyl alcohol* was obtained in 64% yield from *m*-chlorobenzaldehyde and magnesium  $\beta$ -phenylethyl bromide in ethereal solution. It boiled at 210—215°/25 mm. (Found: Cl, 14.65.  $C_{15}H_{15}OCl$  requires Cl, 14.45%).

*$\gamma$ -Phenyl- $\alpha$ -m-chlorophenylpropyl bromide* was obtained from the alcohol in 43% yield, and boiled at 200—205°/30 mm. (0.2258 g.

gave 0.2457 g. of AgCl + AgBr.  $C_{15}H_{14}ClBr$  requires 0.2435 g. of AgCl + AgBr).

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