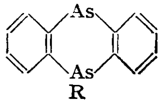
134. *A Synthesis of Derivatives of* o-*Phenylene-ethylenediarsine and of* o-*Phenylenetrimethylenediarsine.*

By R. H. Glauert and Frederick G. Mann.

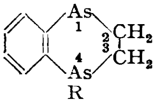
Derivatives of the above two novel heterocyclic ring systems can readily be obtained from *o*-phenylenebisdimethylarsine, which combines with ethylene dibromide to give 1 : 1 : 4 : 4-tetramethyl-*o*-phenylene-ethylenediarsonium dibromide, and with trimethylene dibromide to give 1 : 1 : 5 : 5-tetramethyl-*o*-phenylenetrimethylenediarsonium dibromide. The thermal decomposition of these salts is being investigated.

In view of the fact that the heterocyclic ring system of the 5 : 10-disubstituted 5 : 10-dihydroarsanthrens (I) can be reasonably readily synthesised and has high stability (Kalb, *Annalen*, 1921, **423**, 74; Chatt and Mann, *J.*, 1940, 1184), it is surprising that the similar but simpler systems present in the 1 : 4-disubstituted *o*-phenylene-ethylenediarsines (1 : 4-diarsatetrahydronaphthalenes) (II) and in the 1 : 4-disubstituted diethylenediarsines (1 : 4-diarsa*cyclo*hexanes) (III) have hitherto not been recorded. We are engaged in the systematic study of the systems (II) and (III) and of their derivatives, and the present paper records briefly one ready synthesis of the heterocyclic system (II) and of analogous compounds.

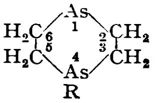
For this synthesis we have utilised *o*-phenylenebisdimethylarsine (IV), prepared by the method of Chatt and Mann (*J.*, 1939, 610). This diarsine appeared to be particularly promising



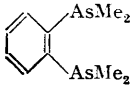
(I.)



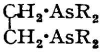
(II.)



(III.)



(IV.)

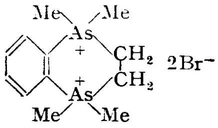


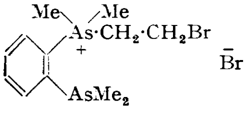
$$\begin{matrix} CH_2\cdot AsR_2 \\ | \\ CH_2\cdot AsR_2 \end{matrix}$$

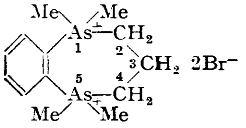
(V.)

for our purpose, for the two tertiary arsine groups are known to be highly reactive, since Chatt and Mann (*J.*, 1939, 1622) and Allison and Mann (*J.*, 1949, 2915) have shown that the diarsine has strongly chelating properties. Furthermore, it was considered that a diarsine of this type would lend itself more readily to the projected cyclisation than, for example, the corresponding ethylenebisdialkylarsines (V) (Chatt and Mann, *loc. cit.*), because in the former compound the two tertiary arsenic atoms are held rigidly by the *o*-phenylene group in precisely the position required for ring formation.

Experiment has confirmed these considerations. We find that, when the diarsine (IV) is heated with one molecular equivalent of ethylene dibromide, combination readily occurs to give the highly crystalline *dimethobromide* (VI) of 1 : 4-dimethyl-*o*-phenylene-ethylenediarsine, *i.e.*, 1 : 1 : 4 : 4-*tetramethyl*-o-*phenylene-ethylenediarsonium dibromide* (1 : 1 : 4 : 4-*tetramethyl*-1 : 2 : 3 : 4-*etrahydro*-1 : 4-*diarsonianaphthalene dibromide*), m. p. 255°. Evidence that cyclisation has in fact occurred and that the product is not the isomeric monoarsonium bromide (VII) is provided in two ways : (*a*) volumetric analysis of a cold aqueous solution of the compound shows that all the bromine is present in the ionic form, and (*b*) the addition of aqueous sodium picrate to such a solution causes the immediate precipitation of the corresponding *dimethopicrate*.


(VI.)


(VII.)


(VIII.)

This type of cyclisation is not limited to the formation of six-membered ring systems. We find that the diarsine (IV) when similarly heated with trimethylene dibromide readily gives the highly crystalline bicyclic *dimethobromide* (VIII), *i.e.*, 1 : 1 : 5 : 5-*tetramethyl-o-phenylenetrimethylenediarsonium dibromide* (1 : 1 : 4 : 4-*tetramethyl*-1 : 4-*diarsonia*-2 : 3-*benz*cyclo*hept*-2-*ene dibromide*), m. p. 258°. Here again cyclisation is confirmed by determination of ionic bromine, and by conversion of the dibromide in cold aqueous solution into the corresponding *dimethopicrate*. There is little doubt that, particularly in the seven-membered ring system present in the compound (VIII), the polymethylene chain is " buckled " and that a stable and probably almost strainless ring is thus produced.

It is significant that both the dimethobromides (VI) and (VIII) melt with effervescence. A preliminary investigation of the thermal decomposition of the dimethobromide (VI) indicates that more than one tertiary arsine may thus be formed. We are now investigating this decomposition on a larger scale because the expected simple loss of methyl bromide would give rise to 1 : 4-dimethyl-*o*-phenylene-ethylenediarsine, which should then be capable of conversion into a tricyclic diarsine system by further combination with ethylene dibromide—a synthesis which would be precisely analogous to Mann and Mukherjee's synthesis of the dimethobromide of triethylenediamine by the combination of 1 : 4-dimethylpiperazine and ethylene dibromide (*J.*, 1949, 2298).

EXPERIMENTAL.

o-*Phenylenebisdimethylarsine* (IV).—By working in an atmosphere of nitrogen, as Chatt and Mann (*loc. cit.*) recommend, this diarsine was prepared from *o*-phenylenebisdichloroarsine, in 82% yield, as a colourless liquid, b. p. 146°/15 mm.

1 : 1 : 4 : 4-*Tetramethyl*-o-*phenylene-ethylenediarsonium Dibromide* (1 : 1 : 4 : 4-*Tetramethyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 4-*Diarsonianaphthalene Dibromide*) (VI).—A mixture of the diarsine (IV) (2·7 g.) and dry ethylene dibromide (1·8 g., 1 mol.) was heated under nitrogen at 125—130°, *i.e.*, at just below the b. p. of the dibromide. The mixture soon solidified and after a further 2 hours' heating was cooled, pulverised, washed with ether, and recrystallised from methyl alcohol. The *dibromide* (VI) was obtained as white crystals, m. p. 255° (effervescence) (Found : C, 30·1; H, 4·8; ionic Br, 33·0. $C_{12}H_{20}Br_2As_2$ requires C, 30·4; H, 4·3; ionic Br, 33·7%). The dibromide is freely soluble in cold water, moderately soluble in boiling methyl alcohol, but only sparingly soluble in boiling ethyl alcohol.

When a cold aqueous solution of the dibromide was added to a similar solution of sodium picrate in excess, an immediate precipitation of the *dipicrate* occurred. This salt, when collected, washed, and recrystallised from water, formed yellow crystals, m. p. 236—238° (Found : C, 37·7; H, 3·3; N, 10·6. $C_{24}H_{24}O_{14}N_6As_2$ requires C, 37·4; H, 3·1; N, 10·9%).

1 : 1 : 5 : 5-*Tetramethyl*-o-*phenylenetrimethylene-diarsonium Dibromide* (1 : 1 : 4 : 4-*Tetramethyl*-1 : 4-*diarsonia*-2 : 3-*benz*cyclo*hept*-2-*ene Dibromide*) (VIII).—This compound was prepared similarly to the previous dibromide, from the diarsine (6·1 g.) and trimethylene dibromide (2·15 c.c., 1 mol.) at 156—160°. Formation of a solid product first became apparent when the bath-temperature reached 135°. The *dibromide*, after recrystallisation from methyl alcohol, formed colourless hygroscopic crystals, m. p. 258° (effervescence) (Found : C, 32·0; H, 4·5; ionic Br, 32·6. $C_{13}H_{22}Br_2As_2$ requires C, 32·0; H, 4·5; ionic Br, 32·8%). This dibromide is freely soluble in cold water, but only very slightly soluble in boiling ethyl alcohol. A mixture of this compound and the dibromide (VI) had m. p. 248° (effervescence).

The corresponding *dipicrate*, prepared as before from a cold aqueous solution of the dibromide differed from the previous dipicrate in that it was almost insoluble in boiling water, methyl and ethyl alcohols. It was therefore collected, washed with water, and dried, and thus obtained as a yellow powder, m. p. 260° (Found: C, 38·5; H, 3·5; N, 10·7. $C_{25}H_{26}O_{14}N_6As_2$ requires C, 38·25; H, 3·3; N, 10·7%).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[*Received, November 24th,* 1949.]