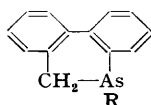


392. The Synthetic Application of Phenylarsinebis(magnesium Bromide). Part II. The Synthesis and Properties of 6-Substituted 6-Arsa-1 : 2 : 3 : 4-dibenzcyclohepta-1 : 3-dienes.

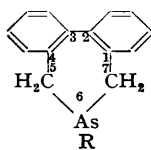
By M. H. BEEBY, FREDERICK G. MANN, and E. E. TURNER.

The synthesis of 6-phenyl-6-arsa-1 : 2 : 3 : 4-dibenzcyclohepta-1 : 3-diene and its conversion by the action of hydriodic acid into the 6-iodo-analogue are described. The probable dimensions of the central heterocyclic ring in these compounds indicate that the two outer benzene rings are locked at an angle of 63° , and that the compounds therefore possess molecular dissymmetry. This absence of co-planarity of the benzene rings is strongly supported by the spectroscopic evidence.

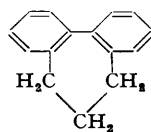
THE preparation and properties of 10-substituted 9 : 10-dihydroarsanthridines (I) have recently been recorded by Cookson and Mann (*J.*, 1949, 2888), who showed that a calculation based on accepted bond-lengths and atomic radii indicated that the dimensions of the central heterocyclic ring excluded the possibility of a planar molecule, and that the two benzene rings subtended an angle of *ca.* 34° . On the other hand, the spectroscopic evidence indicated a certain degree of oscillation of the benzene rings about the planar position, since two of these compounds showed an absorption band which was probably the characteristic absorption band of diphenyl slightly displaced and reduced in intensity. The diphenyl band is considered to owe its origin to excited states arising from ionic structures in all of which the two benzene rings of diphenyl are linked by a double bond and are hence coplanar; the reduced intensity of this band in the dihydroarsanthridines would thus imply a certain oscillation about this coplanar position.



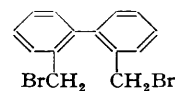
(I.)



(II.)



(III.)



(IV.)

In view of these results, considerable interest attached to compounds of type (II), in which the heterocyclic ring has been increased by the addition of another CH_2 group; such compounds can be regarded systematically as derivatives of 1 : 2 : 3 : 4-dibenzcyclohepta-1 : 3-diene (III), and hence are termed 6-substituted 6-arsa-1 : 2 : 3 : 4-dibenzcyclohepta-1 : 3-dienes. The ready preparation of 2 : 2'-bisbromomethyldiphenyl (IV) by the method of Hall, Leslie, and Turner (*J.*, 1950, 711) provides a simple approach to compounds of type (II), for we find that the dibromo-compound (IV) reacts smoothly with phenylarsinebis(magnesium bromide) to give 6-phenyl-6-arsa-1 : 2 : 3 : 4-dibenzcyclohepta-1 : 3-diene (II; $\text{R} = \text{Ph}$), a crystalline compound of m. p. $118-118.5^\circ$, and also phenyldibromoarsine as a by-product. The former compound is the first to be isolated having a seven-membered ring consisting solely of carbon and one arsenic atom, although compounds containing a seven-membered ring consisting of carbon and two arsenic atoms are known (Glauert and Mann, *J.*, 1950, 682). The heterocyclic ring in the 6-phenyl compound (II; $\text{R} = \text{Ph}$) has however considerable stability, because treatment with boiling hydriodic acid replaces the phenyl group by an iodo-group without affecting the ring, and thus gives 6-iodo-6-arsa-1 : 2 : 3 : 4-dibenzcyclohepta-1 : 3-diene, pale yellow crystals, m. p. $117-117.5^\circ$. Further action by a Grignard agent would clearly in turn replace the iodo-group with any desired alkyl or aryl group. This fission of a phenyl group directly attached to an arsenic atom which is part of a ring system, without injury to the system itself, appears to be widespread: it has already been shown to occur in the *iso*arsindolines, the 1 : 2 : 3 : 4-tetrahydro*iso*arsindolines, and the 2-arsaperinaphthanes (*J.*, 1947, 662; 1950, 1917).

A study of the stereochemistry of molecules of type (II) reveals several points of interest. If the bond-lengths and the atomic radii utilised by Cookson and Mann (*loc. cit.*) are applied to the tricyclic ring system (II), and an intervalency angle of 100° at the arsenic atom is accepted (cf. Chatt and Mann, *J.*, 1940, 1184), calculation shows that the two benzene rings subtend an angle of 63° ; moreover the intervalency angle within the ring at carbon atoms 5 and 7 becomes 110° , and the ring is presumably almost strainless. A model based on these dimensions

shows that the central heterocyclic ring locks the two non-planar benzene rings in position, and that no rotation of them about their common axis is possible. When the tertiary arsine forms a quaternary salt, *e.g.*, the monomethiodide of 6-phenyl-6-arsa-1 : 2 : 3 : 4-dibenzcyclohepta-1 : 3-diene (alternatively named 6-phenyl-6-methyl-6-arsonia-1 : 2 : 3 : 4-dibenzcyclohepta-1 : 3-diene iodide) (V), the intervalency angle within the ring of the arsenic atom almost certainly increases to *ca.* 109°; since however there will be a simultaneous shrinkage of the interatomic As-C distance, the process will probably be without notable effect on the angle between the two benzene rings and on the stability of the heterocyclic ring.

Spectroscopic evidence confirms these considerations. In Fig. 1 there are shown for comparative purposes: the absorption spectrum of diphenyl (A), having the characteristic band at 248 $m\mu$., ϵ_{\max} 17,000, due to the coplanar rings; the spectrum of 10-phenyl-10-methyl-9 : 10-dihydroarsanthridinium iodide (B), having the band at 269 $m\mu$., ϵ_{\max} 9,600 (Cookson and Mann, *loc. cit.*); and the spectrum of 6-phenyl-6-methyl-6-arsonia-1 : 2 : 3 : 4-dibenzcyclo-

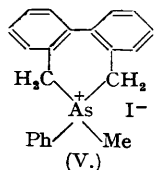
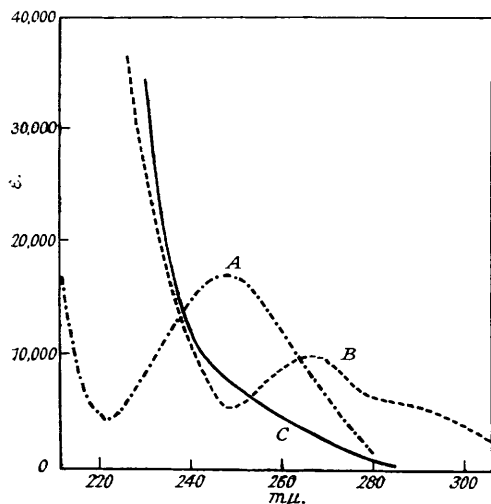
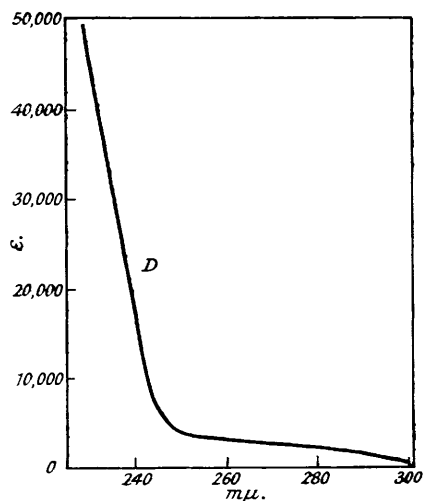


FIG. 1.



(A) Diphenyl. (B) 10-Phenyl-10-methyl-9 : 10-dihydroarsanthridinium iodide. (C) 6-Phenyl-6-methyl-6-arsonia-1 : 2 : 3 : 4-dibenzcyclohepta-1 : 3-diene iodide.

FIG. 2.



6-Iodo-6-arsa-1 : 2 : 3 : 4-dibenzcyclohepta-1 : 3-diene.

hepta-1 : 3-diene iodide (V) (C), in which this band is entirely absent. Fig. 2 gives the absorption spectrum of the 6-iodo-derivative (II; R = I); this also shows no sign of the diphenyl band, and the absence of rotation about the common axis of the two benzene rings in those compounds is thus strikingly confirmed. It is noteworthy that the spectra of the quaternary methiodide (V) and the 6-iodo-compound (II; R = I) although closely similar are not identical, wherein they differ from those of the analogous derivatives in the 2-arsaperinaphthane series, which are almost completely identical (*cf.* previous paper).

The twisted heterocyclic ring in compounds of type (II) causes these tertiary arsines to possess molecular dissymmetry: the formation of a quaternary salt such as (V), having two dissimilar groups joined to the arsenic atom, does not produce an asymmetric arsenic atom, but the molecular dissymmetry of course persists. Such compounds should therefore be resolvable into optically active forms, a possibility which is now being investigated.

EXPERIMENTAL.

6-Phenyl-6-arsa-1 : 2 : 3 : 4-dibenzcyclohepta-1 : 3-diene (II; R = Ph).—A solution of 2 : 2'-bis-bromomethyldiphenyl (IV) (8 g.) in benzene (30 c.c.) was added to the chilled and agitated ether-benzene solution of the arsine-Grignard reagent prepared from phenylarsine (3.65 g., 1 mol.) (see preceding paper). The complete mixture was stirred at room temperature for 30 minutes and then boiled under reflux for 1 hour. After cooling and hydrolysis with ammonium chloride solution, the organic layer was separated, dried, and evaporated. The semi-solid residue, when recrystallised from alcohol, gave the *arsine* (II; R = Ph) (3.55 g., 45%), m. p. 112–115°, increased to 118–118.5° by further recrystallisation (Found :

C, 71.8; H, 5.2; *M*, ebullioscopic in 1.486% alcoholic solution, 342. $C_{20}H_{17}As$ requires C, 72.3; H, 5.2%; *M*, 332). The alcoholic mother-liquor contained phenyldibromoarsine, for when treated with piperidine *N*-pentamethylenedithiocarbamate it deposited phenylarsinebis-(*N*-pentamethylenedithiourethane), which after purification had m. p. 175—176°, unchanged by admixture with an authentic sample.

A mixture of the arsine and methyl iodide was boiled under reflux for 30 minutes and then evaporated. Recrystallisation of the residue from methyl alcohol gave *6-phenyl-6-methyl-6- arsonia-1:2:3:4-dibenzcyclohepta-1:3-diene iodide* (V) as a *monomethanolate* which on heating lost methyl alcohol at ca. 104° (Found: C, 51.9; H, 4.8. $C_{21}H_{20}IAs, CH_4O$ requires C, 52.2; H, 4.8%). After 2 hours' heating at 128°/0.1 mm. the solvent-free iodide, m. p. 223—224° (preliminary darkening) was obtained (Found: C, 53.15; H, 4.3. $C_{21}H_{20}IAs$ requires C, 53.2; H, 4.25%).

When a benzene solution containing equimolecular quantities of the arsine and *p*-chlorophenacyl bromide was boiled under reflux for 1 hour and cooled, colourless crystals of *6-phenyl-6-p-chlorophenacyl-6- arsonia-1:2:3:4-dibenzcyclohepta-1:3-diene bromide* separated. Recrystallisation from alcohol-benzene gave crystals which retained benzene even when heated at 60°/0.1 mm. for 2 hours; heating at 100°/0.1 mm. for 3 hours ultimately gave the solvent-free but rather glassy bromide, m. p. ca. 110—115° (Found: C, 59.0; H, 4.0. $C_{28}H_{22}OClBrAs$ requires C, 59.4; H, 4.1%).

A mixture of the arsine and hydriodic acid of constant b. p. was boiled under reflux for 2 hours in a carbon dioxide atmosphere. The liquid was decanted from the cold product, and the solid residue, when washed with water and recrystallised first from alcohol and then from light petroleum (b. p. 80—100°), gave *6-iodo-6-arsa-1:2:3:4-dibenzcyclohepta-1:3-diene* (II; R = I) as yellow crystals, m. p. 117—117.5° (Found: C, 44.2; H, 3.2. $C_{16}H_{12}IAs$ requires C, 44.0; H, 3.2%).

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