

226. *The Preparation and Properties of 1-Phenyl-1-phospha-2:3-6:7-dibenzocyclohepta-2:6-diene and its Arsenic Analogue.*

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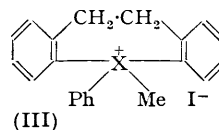
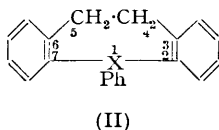
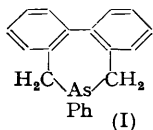
The tertiary phosphine and arsine named in the title have been prepared by the action of 2:2'-dilithiodibenzyl on phenyldichloro-phosphine and -arsine respectively. The compounds show isodimorphism: each exists in a low- and a high-melting form, the two low-melting and the two high-melting forms constituting isomorphous pairs.

The chemical properties, and also the absorption spectra of the above compounds and their methiodides, are discussed.

THE synthesis of 6-phenyl-6-arsa-1:2-3:4-dibenzocyclohepta-1:3-diene (I) has recently been described by Beeby, Mann, and Turner (*J.*, 1950, 1923), who calculated that in this compound the two *o*-phenylene groups subtend an angle of *ca.* 63°: this conclusion received confirmation from the fact that the absorption spectra of the 6-phenyl and the 6-iodo-compounds were entirely free from the characteristic diphenyl band at 248  $\mu$ , which would be shown only when these two groups approach coplanarity.

We have now prepared the isomeric 1-phenyl-1-arsa-2:3-6:7-dibenzocyclohepta-2:6-diene (II; X = As) and the analogous 1-phospha-derivative (II; X = P) in order to investigate their spectra: these compounds, being essentially a triaryl-arsine and -phosphine, are of course entirely different in type from (I).

2:2'-Dibromodibenzyl,  $\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{Br}$ , has been isolated by Beeby and Mann (*J.*, 1951, 411) as a by-product in the formation of *o*-bromobenzylmagnesium bromide, but we find that even under the most favourable conditions the yield is impractically low. For this preparation we have therefore considerably improved the method of Kenner and Wilson (*J.*, 1927, 110), whereby *o*-bromobenzyl bromide is converted by hydrazine into 1:1-di-*o*-bromobenzylhydrazine ( $\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ )<sub>2</sub>N·NH<sub>2</sub>, which on oxidation with mercuric oxide furnishes 2:2'-dibromodibenzyl.



Our attempts to convert this dibromodibenzyl into a di-Grignard reagent failed, although a variety of conditions were employed. *n*-Butyl-lithium however readily gave 2:2'-dilithiodibenzyl, which readily reacted with phenyldichlorophosphine to give 1-phenyl-1-phospha-2:3-6:7-dibenzocyclohepta-2:6-diene (II; X = P) as colourless crystals. It is of interest that this compound, when isolated from the crude reaction product by fractional distillation followed by recrystallisation, was for many weeks stable when exposed to the air at room temperature either in the solid state or in methanolic solution. When, alternatively, the crude distillate was converted into the methiodide (III; X = P) and the latter purified by recrystallisation, heating at 340°/0.001 mm. was required before dissociation of the salt gave the phosphine as a syrup, which, however, was then so susceptible to oxidation that attempted recrystallisation gave solely the phosphine oxide. It is possible that traces of iodine catalytically promote this very ready oxidation.

2:2'-Dilithiodibenzyl reacted similarly with phenyldichloroarsine to form the 1-arsa-compound (II; X = As) which was also isolated both by distillation and subsequent crystallisation, and by distillation followed by conversion into the methiodide (III; X = As): the latter underwent ready dissociation at 260°/0.001 mm. and the arsine thus obtained, when purified by recrystallisation, was as stable as that prepared by the first method.

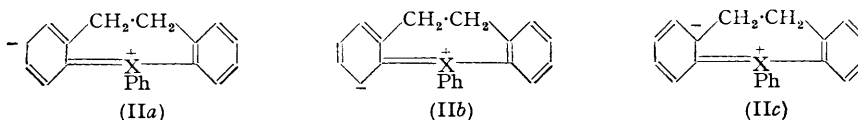
The phosphine and the arsine provide a very interesting example of the comparatively rare phenomenon of isodimorphism. These compounds, when prepared as described

above, had m. p.s 75—75.5° and 59—59.5° respectively, which were retained unchanged throughout several weeks of laboratory manipulation. A crude distilled syrupy sample of the freshly prepared phosphine solidified readily when seeded with the arsine, with which it is almost certainly isomorphous. However, in later experiments to test the stability of the heterocyclic ring, the phosphine was heated under reflux with hydriodic acid under nitrogen for 2 hours: the ring was unaffected and only an unstable hydriodide of the phosphine was isolated. This salt when hydrolysed by warm aqueous ethanol deposited however the free phosphine which after recrystallisation had m. p. 94.5—95°. When a trace of this more stable modification was either triturated with crystals of the earlier form, or added to the molten phosphine at 80°, the m. p. of the mixture rose to 94.5—95°: both forms, however, gave the same methiodide.

Furthermore, a molten sample of the arsine at 65°, when seeded with a trace of the high-melting phosphine, rapidly solidified and after recrystallisation from ethanol had m. p. 78.5—79°: this higher-melting form of the arsine could now be similarly used for the conversion of other samples of the lower-melting form. Again, both forms of the arsine gave the same methiodide. There is very little doubt therefore that each form of the phosphine is isomorphous with the corresponding form of the arsine.

It is noteworthy that the chemical stability of the phosphine towards boiling hydriodic acid is not shared by the arsine, which was converted by this treatment into dibenzyl and arsenic tri-iodide. This behaviour is similar to that of tri-*p*-methoxyphenylarsine, which Michaelis and Weitz (*Ber.*, 1887, 20, 48) showed was ultimately converted into anisole and arsenic tri-iodide. It is, however, in striking contrast to 2-phenylisoarsindoline, 2-phenylarsaperinaphthane, 6-phenyl-6-arsa-1 : 2-3 : 4-dibenzocyclohepta-1 : 3-diene, and hexahydro-1 : 4-diphenyl-1 : 4-arsazine, in all of which the hydriodic acid treatment caused the phenyl group directly joined to the arsenic to be replaced by an iodo-group without, however, any fission of the heterocyclic ring (Mann and his co-workers, *J.*, 1947, 662; 1950, 1917, 1923; 1951, 886). In these four compounds, however, the arsine is systematically a dialkylmonoaryarsine, whereas our present arsine (II; X = As) is a triaryarsine. It appears from these examples that this type of fission is limited to aryl groups directly joined to arsenic.

In view of the triaryl nature of the phosphine and arsine (II; X = P and As), considerable interest attaches to a comparison of their absorption spectra with those of their triphenyl analogues. (In both Figs. 1 and 2, the scale of  $\log_{10} \epsilon$  values for the phosphorus compounds has been raised above that of the arsenic compounds to avoid overmuch superposition of the curves.) It will be seen in Fig. 1 that the spectrum of the phosphine (II; X = P) is closely similar to that of triphenylphosphine, and that of the arsine (II; X = As) also to that of triphenylarsine, all four compounds showing only one broad absorption band. If any of these four compounds possessed three independently absorbing benzenoid rings, several absorption bands would be expected, with the main absorption at about  $\lambda_{\max}$ , 255 m $\mu$ ,  $\log_{10} \epsilon_{\max}$ , 2.8. The absence of these individual bands and the greater intensity indicate considerable resonance from the numerous forms such



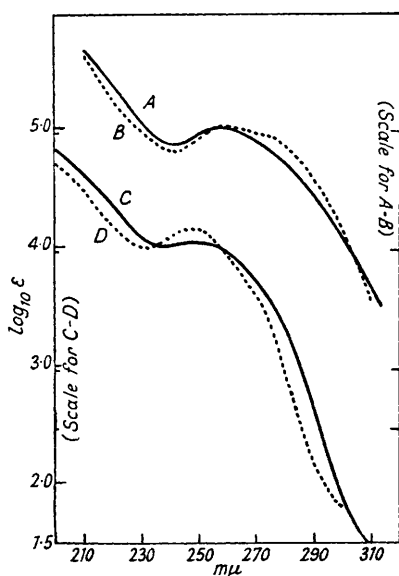
as (IIa), (IIb), and (IIc), a type of resonance which clearly will be little affected by the  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot$  chain joining two of the benzene rings: hence it would be expected that the members of each pair of compounds would have very similar spectra.

In Fig. 2 are shown the spectra of the methiodides of the above four compounds: in these salts the positive charges on the phosphorus and the arsenic atoms prevent resonance of the above type, and the main absorptions have now considerably lower intensities. The interesting feature is now however the very close resemblance between the spectra of the methiodides of the phosphine and arsine (II; X = P and As) and between those of the methiodides of triphenyl-phosphine and -arsine, the change of the hetero-atom having very little effect. It is probable that the several bands in the region 250—280 m $\mu$  shown

by the methiodides of triphenyl-phosphine and -arsine represent the normal absorption of the benzene groups, which are apparently merged into one main broad absorption in the heterocyclic methiodides.

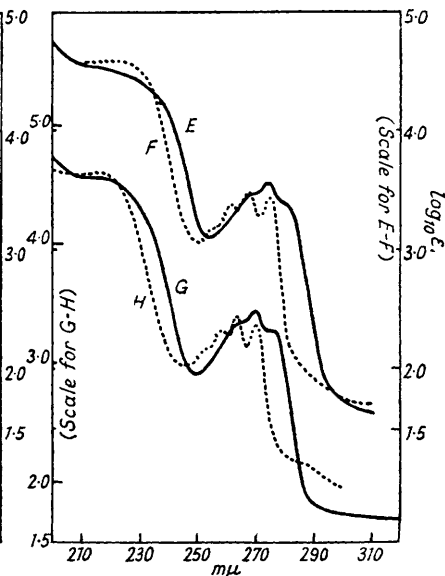
It is noteworthy that Bowden and Braude (*J.*, 1952, 1068) have shown that dimethyl-phenyl-phosphine and -arsine both show one broad absorption band, whereas the methiodides of these compounds show four bands between 250 and 272  $m\mu$ , which they describe as "resembling that of benzene in the 250  $m\mu$  region." The spectra of their compounds thus show a strong general resemblance to those which we have obtained for triphenyl-phosphine and -arsine and their methiodides respectively.

FIG. 1.



A, The phosphine (II; X = P).  
B, Triphenylphosphine.  
C, The arsine (II; X = As).  
D, Triphenylarsine.

FIG. 2.



E, Methiodide of the phosphine (II; X = P).  
F, " triphenylphosphine.  
G, " the arsine (II; X = As).  
H, " triphenylarsine.

#### EXPERIMENTAL

Consistent values for certain m. p.s could be obtained only if they were determined in evacuated tubes: these are denoted (E. T.).

**2: 2'-Dibromodibenzyl.**—The following preparation is based on that by Kenner and Wilson (*loc. cit.*) who give very little detail of their small-scale work.

**1: 1-Di-*o*-bromobenzylhydrazine hydrochloride.** A solution of *o*-bromobenzyl bromide (325 g.) in ethanol (750 c.c.) was added during 1 hour to pure hydrazine hydrate (100 g.) in ethanol (225 c.c.), with stirring and under a condenser. During the addition, hydrazine hydrobromide separated as an oil which solidified if the mixture was allowed to cool. The ethanol was then distilled, and water (1750 c.c.) added to the residue which was extracted with ether (1 l.; then 2 × 300 c.c.). The united, dried, filtered extracts were diluted with a solution of saturated ethanolic hydrogen chloride (50 c.c.) in ethanol (400 c.c.), whereby the required hydrochloride was precipitated. The latter was at once collected, and purified by dissolution in boiling ethanol (1 l.), cooling, and reprecipitation by ether (1900 c.c.). The purified product was collected, washed with ether, and dried in a vacuum (m. p. 211–212°; 91 g., 34%). The ethanolic hydrogen chloride mother-liquor when set aside deposited crude tri-*o*-bromobenzylhydrazine hydrochloride.

**Oxidation.** The hydrochloride (90 g.) was shaken with 5% aqueous sodium hydroxide (200 c.c.), which was then extracted with chloroform (2 × 150 c.c.). The combined extracts were dried (Na<sub>2</sub>SO<sub>4</sub>), and the hydrazine was oxidised by the addition of finely powdered yellow mercuric oxide (60 g.), in portions (10 g.) during 1 hour, to the vigorously stirred solution,

nitrogen being evolved. The mixture was stirred for a further 3 hours, then filtered, and the solvent evaporated. The residue, which completely solidified on cooling, could not be purified satisfactorily by recrystallisation alone. Distillation however gave the 2 : 2'-dibromodibenzyl as a fraction, b. p. 138—148°/0.013 mm., which rapidly solidified, and when recrystallised from ethanol formed colourless crystals, m. p. 83—84° (38.5 g., 51%). The crude product probably contained some di-*o*-bromobenzylmercury, because during the distillation metallic mercury was liberated.

*n*-Butyl-lithium.—This was prepared under nitrogen by the method of Gilman, Langham, and Moore (*J. Amer. Chem. Soc.*, 1940, **62**, 2327), with however light petroleum of b. p. 40—45° instead of that of b. p. 28—38°. Before use, the concentration of the reagent was determined by titration with N/10-hydrochloric acid (methyl-orange).

1-Phenyl-1-*phospha-2 : 3-6 : 7-dibenzocyclohepta-2 : 6-diene* (II; X = P).—This preparation was performed in a flask fitted with a sealed stirrer, reflux condenser, dropping funnel, and an inlet tube through which nitrogen passed throughout the experiment. Solutions of 2 : 2'-dibromodibenzyl (15.3 g.) in light petroleum (b. p. 40—45°; 300 c.c.) and of *n*-butyl-lithium (2.2 mols. : 112 c.c. of 0.882N-solution, also in this petroleum) were mixed, boiled under reflux for 12 hours, set aside overnight, and then chilled in ice-water whilst a solution of phenyl-dichlorophosphine (8.06 g., 1 mol.) in benzene (150 c.c.) was added with stirring during 30 minutes. The mixture was then boiled for 3 hours, again chilled, and hydrolysed with air-free water (200 c.c.). The organic layer was collected, dried (Na<sub>2</sub>SO<sub>4</sub>), and freed from solvent, and the residue distilled at 0.01 mm., giving the fractions: (a) b. p. 150—170° (*ca.* 5 g.); readily solidified; mainly 2 : 2'-dibromodibenzyl; (b) b. p. 170—190°; a pale amber syrup (4 g.) which solidified when stirred with ethanol and then seeded with the arsine, m. p. 59° (see later), and when then twice recrystallised from ethanol gave the phosphine as colourless crystals, m. p. 75—75.5° (3 g., 23%) (Found: C, 83.3; H, 5.8; *M*, ebullioscopic in 0.859% ethanol solution, 289. C<sub>20</sub>H<sub>11</sub>P requires C, 83.3; H, 5.95%; *M*, 288); (c) b. p. 190—230°; a viscous liquid which formed a milky glass (*ca.* 4 g.). This fraction could not be crystallised and did not form a crystalline methiodide: it probably consisted mainly of a linear polymeric phosphine, contaminated with the above cyclic phosphine. The fraction was repeatedly extracted with petroleum (b. p. 60—80°) and the united extracts, when evaporated in the air, deposited a gum which on recrystallisation from ethanol gave in small yield the phosphine oxide, m. p. 173—174°, undepressed by admixture with that described below.

The phosphine (II; X = P) did not form a stable hydrochloride or a picrate.

*Methiodide.* The fraction (b) dissolved readily in methyl iodide with heat evolution and subsequent deposition of the *methiodide*, colourless crystals (from ethanol), m. p. 251—252° (E. T.) (Found: C, 58.75; H, 4.9. C<sub>21</sub>H<sub>20</sub>IP requires C, 58.65; H, 4.7%). The thermal stability of this salt is markedly greater than that of its arsenic analogue. For example, a sample was heated in nitrogen at 300—310°/0.001 mm. for 30 minutes, and the residue when recrystallised from ethanol gave the unchanged methiodide in high yield: the ethanolic mother-liquor contained some free phosphine mixed with the unchanged methiodide, for, when boiled with an excess of potassium palladochloride, it afforded *di-iodobisphosphine-μ-di-iodopalladium*, chocolate-brown crystals, m. p. 283—285° (decomp.), from ethanol (Found: C, 36.75; H, 2.45. C<sub>40</sub>H<sub>34</sub>I<sub>4</sub>P<sub>2</sub>Pd<sub>2</sub> requires C, 37.0; H, 2.6%). When the methiodide was similarly heated at 340—345°, decomposition occurred, but the gummy distillate when recrystallised from methanol gave the colourless *oxide*, m. p. 173.5—174.5° (Found: C, 78.45; H, 5.45. C<sub>20</sub>H<sub>11</sub>OP requires C, 78.9; H, 5.6%). The pure phosphine, obtained by direct crystallisation of fraction (b) above, was however unchanged after exposure to the air for 14 days, and its methanolic solution when similarly exposed deposited large crystals of the unchanged phosphine, m. p. 75.0—75.5° (mixed and unmixed).

An ethanolic solution of the phosphine, when boiled with aqueous potassium palladochloride, deposited the *dichlorobisphosphinepalladium*, which separated from dioxan as fine yellow crystals, m. p. 278—280°, which even after heating at 100°/0.1 mm. for 8 hours still retained dioxan of crystallisation (Found: C, 62.7; H, 4.9. C<sub>40</sub>H<sub>34</sub>Cl<sub>2</sub>P<sub>2</sub>Pd, C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> requires C, 62.7; H, 5.0%).

*Action of hydriodic acid.* A mixture of the phosphine (0.1 g.) of m. p. 75—75.5° and pure hydriodic acid (30 c.c.) of constant b. p. was boiled under reflux in nitrogen for 2 hours, a clear solution being obtained without other apparent change. Evaporation under nitrogen then gave an oily residue which crystallised when cooled and scratched. These colourless crystals (which were apparently a crude hydriodide) were very soluble in water, but could not be recrystallised from any common solvent without decomposition: at room temperature they very rapidly decomposed with liberation of iodine, and when heated they melted indefinitely.

## 1134 1-Phenyl-1-phospha-2 : 3-6 : 7-dibenzocyclohepta-2 : 6-diene, etc.

An aqueous ethanolic solution, when boiled and cooled, deposited the high-melting form of the phosphine as colourless crystals, m. p. 94.5—95° after two recrystallisations from ethanol (Found : C, 83.5; H, 6.2%).

Within a few days of the first isolation of this form, it was found that the low-melting form, when heated in a sealed capillary tube still melted at 75—75.5°, but when heated in an open tube started to soften at 75° and then before fusion was complete started to resolidify from the top downwards, becoming completely solid at 80° and finally melting sharply at 95—95.5°.

1-Phenyl-1-arsa-2 : 3-6 : 7-dibenzocyclohepta-2 : 6-diene (II; X = As).—This was prepared precisely as the analogous phosphine, by using 2 : 2'-dibromodibenzyl (10.2 g.) in light petroleum (200 c.c.), *n*-butyl-lithium (2.2 mols., 68 c.c. of 0.97*N*), and phenyldichloroarsine (6.7 g., 1 mol.) in benzene (100 c.c.). After removal of the solvent, distillation at 0.15 mm. gave the fractions : (a) b. p. 115—155°, 0.8 g.; (b) b. p. 155—180°, 0.7 g.; and (c) b. p. 180—183°, 2.2 g. Fraction (c) completely crystallised, whereas (a) and (b) remained semi-solid. A portion of (c), when recrystallised from ethanol, gave the pure arsine (II; X = As). To conserve material, however, these fractions were dissolved together in methyl iodide, and rapidly deposited the colourless *methiodide* (III; X = As) (1.7 g.), m. p. 215—227° (E.T.) after recrystallisation from ethanol (Found : C, 52.6; H, 4.25. C<sub>21</sub>H<sub>20</sub>IAs requires C, 53.2; H, 4.25%). The undistilled residue, when boiled with methyl iodide, gave a second crop (2.7 g.) of the *methiodide*. This salt is slightly soluble in hot water, readily so in cold methanol, and sparingly so in ethanol; the wide melting range was shown by several preparations and is apparently characteristic.

The *methiodide* (0.95 g.), when heated in nitrogen at 260°/0.001 mm., decomposed giving a pale yellow distillate which crystallised when cooled and scratched; recrystallisation from ethanol gave the colourless *arsine* (II; X = As), m. p. 59—59.5° (0.45 g., 75%) (Found : C, 72.3; H, 4.9. C<sub>20</sub>H<sub>17</sub>As requires C, 72.3; H, 5.2%).

An acetone solution of the *arsine*, when treated with an excess of hydrogen peroxide, set aside overnight, and then evaporated, gave a crystalline residue, m. p. ca. 40°, too soluble in common solvents for recrystallisation; when dried at 75°/0.1 mm. for 18 hours, this gave the anhydrous *arsine oxide*, m. p. 188—190° (decomp.) (Found : C, 68.9; H, 5.2. C<sub>20</sub>H<sub>17</sub>OAs requires C, 69.0; H, 4.9%).

The *arsine*, when treated with potassium palladochloride as described for the phosphine, gave the *dichlorobisarsinepalladium*, which crystallised from dioxan as a dark yellow micro-crystalline powder, m. p. 275—277°, which after 1.5 hours at 50°/0.1 mm. still retained solvent of crystallisation (Found : C, 56.85; H, 4.3. C<sub>40</sub>H<sub>34</sub>Cl<sub>2</sub>As<sub>2</sub>Pd.0.5C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> requires C, 56.9; H, 4.3%).

*Action of hydriodic acid.* This was performed precisely as for the above phosphine, but an orange solid began to separate at once on heating. The mixture, after 2 hours' boiling, was concentrated under reduced pressure in nitrogen. The hydriodic acid distillate deposited colourless crystals of dibenzyl which were collected, washed with water, and dried : they had m. p. 52°, unchanged by admixture with an authentic sample. The residue in the flask, when collected and washed with ethanol, afforded orange-red crystals of arsenic tri-iodide, m. p. 139—140°.

*Absorption Spectra.*—These were all determined in ethanolic solution (see Table and Figs.).

	$\lambda_{\max.}$	$\epsilon_{\max.}$	$\lambda_{\min.}$	$\epsilon_{\min.}$		$\lambda_{\max.}$	$\epsilon_{\max.}$	$\lambda_{\min.}$	$\epsilon_{\min.}$
Phosphine (II; X = P) .....	256—257	11,200	242	7800	PPh <sub>3</sub> MeI ...	220—223	39,800	210—216 †	38,700 †
Ph <sub>3</sub> P .....	262—263	11,100	242	6900		261	2,390	249—250	1200
Arsine (II; X = As) .....	246—248	10,680	236	9920	AsPh <sub>3</sub> MeI...	275	2,700	271	2000
Ph <sub>3</sub> As .....	248	13,340	233	9440		216	41,560	205	39,670
<i>Methiodide</i> of (II; X = P) ...	275	3,550	254	1270 *		258	1,890	245	946
<i>Methiodide</i> of (II; X = As)	270	2,730	249	295 *		264	2,440	261	1730
						271	2,060	267	1420

\* Principal values only.

† Inflexion.

The curve for triphenylphosphine closely resembles that of Purvis (*J.*, 1914, 105, 1377), but that of triphenylarsine and of methyltriphenylarsonium iodide differ markedly from those given by Purvis and McClelland (*J.*, 1912, 101, 1514) and Hantzsch (*Ber.*, 1919, 52, 1544) respectively.

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