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^{1}H NMR AND ULTRAVIOLET SPECTRA OF SOME 5,10-DIHYDROPHENARSAZINES AND RELATED COMPOUNDS. EVIDENCE FOR d_π–p_π INTERACTION IN ARSINES AND ARSONIUM COMPOUNDS

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SUMMARY

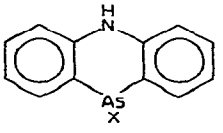
When 5-substituted 5,10-dihydrophenarsazines are converted to their arsonium salts with methyl iodide the NH proton in the ^{1}H NMR spectrum undergoes a downfield shift (4.1–4.2 ppm) too large to be accounted for by inductive effects alone. A similar shift is observed for an (*o*- and a *p*-aminophenyl)arsine but not in an *o*-phenylenediamine. To account for this, d_π–p_π overlap similar to that found in phosphonitrilic compounds is suggested.

The ultraviolet spectra of both the arsines and the arsonium salts are similar and show a long wavelength band (>300 nm) which is attributed to the presence of d_π–p_π bonding in both classes of compound. Again, nitrogen analogues show no comparable effect.

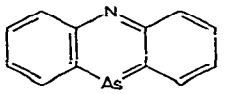
INTRODUCTION

The 5,10-dihydrophenarsazines (I) are the most readily accessible heterocyclic arsenicals and their chemistry was extensively investigated as part of the intense interest in the potential biological uses of organoarsenic compounds[1]. The structure of the parent compound (I; X = Cl) has been the subject of some speculation since its properties (yellow colour, high melting point and sparing solubility in organic solvents) were unexpected for the simple covalent structure. To account for these, ionic structures were suggested[2–4], but the bulk of the evidence is against such an interpretation[1]. In 1965 Cameran and Trotter[5] carried out an X-ray study of the chloroarsine (I; X = Cl) and showed that it did indeed have a covalent structure, though with some unusual features. Thus, the arsenic–carbon bonds are significantly shorter (1.917 ± 0.007 Å) than expected (*cf.* 1.98 Å in 9-phenyl-9-arsafluorene)[6]. Also, the CNC angle (128°) in (I; X = Cl) is larger than normal though the As–Cl distance is the same as in diphenylarsinous chloride. Cameran and Trotter suggested that the anomalous parameters implied electron delocalisation involving the arsenic atom. A number of other systems have been described in the literature in which an arsenic atom is a participant of an extended conjugated system. Kalb described[7] the synthesis of arsanthren (II) and Wieland and Rheinheimer reported[2] the preparation of phenarsazine (III) nearly forty years ago, but since no molecular weight determinations

were carried out there is some doubt as to whether monomers or polymers were obtained. These very interesting substances merit reinvestigation in view of the current great interest in σ-bonding involving elements of the second and higher rows of the periodic table. More recently Mann[8,9] and his collaborators have described a series of compounds whose structures in solution seem to require a formal double bond between arsenic and carbon. The arsanthren derivative (IV) is representative of these and the evidence for this structure is the ionic character of the bromine atoms which may be shown by metathesis with other anions.



(I)



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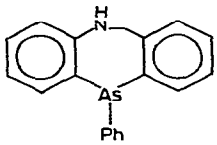
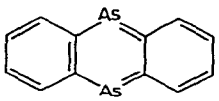
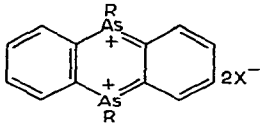


(V)



(II)



(IV)

Our interest in these structures came as part of a synthetic study during which ^{1}H NMR spectra were used to characterise the intermediates. It was observed that the chemical shift difference between the NH proton of the dihydrophenarsazines (I; X=alkyl or aryl) and that in the corresponding arsonium methiodides was unexpectedly large and suggested some type of electron withdrawal from nitrogen by the arsonium centre. To test this hypothesis we have extended the range of compounds as well as synthesizing a number of model compounds, and have measured their ^{1}H NMR and ultraviolet spectra.

RESULTS

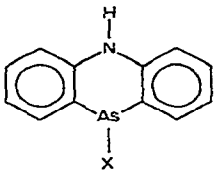
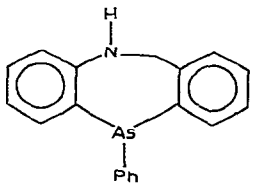
Most of the compounds required were known or readily accessible by standard routes. The synthesis of the azarsepine (V) is described by us elsewhere[10]. To test the effect of replacing arsenic by nitrogen and to gain an idea of the purely electrostatic effect of an adjacent positively charged centre on the chemical shift of the NH proton in a diarylamine, the mixed amine–ammonium salt (VI) was synthesized. *N*,*N*-Dimethyl-*N'*-phenyl-*o*-phenylenediamine (VII) was obtained from *N*-phenyl-*o*-phenylenediamine in the normal way.

$$o\text{-}H_2NC_6H_4NHPh \rightarrow \underset{\text{(VII)}}{o\text{-}Me_2NC_6H_4NHPh} \xrightarrow[\text{tosylate}]{\text{Me-}} \underset{\text{(VI)}}{o\text{-}Me_3\overset{+}{N}C_6H_4NHPhTos^-}$$

Use of dimethyl phosphonate as the alkylating agent[11] gave instead the trimethyl derivative in good yield. An attempt to prepare the amine (VII) directly from aniline and the benzyne obtained by treating *o*-chloro-*N*,*N*-dimethylaniline with sodamide in hexamethylphosphoric triamide[12] gave the *m*-isomer. The desired amine–ammoni-

TABLE 1

CHEMICAL SHIFT (δ) OF NH PROTON OF SOME 5,10-DIHYDROPHENARSAZINES AND RELATED COMPOUNDS[a]

Compound		δ(NH)	Methiodide	
			δ(NH)	$\Delta\delta$(NH)
 (I)	X = CH_3	6.23	10.35[b]	4.12
	X = C_6H_5	6.17	10.40	4.23
	X = o-ClC_6H_4	6.27	10.43	4.16
 (V)		3.91	6.89	2.98
p-Ph_2As—C_6H_4—NHPh (XI)		5.45	9.00[b]	3.55
Ph_2As—CH_2CH_2—NHPh (VIII)		3.48		
$PhMe_2As^+$—CH_2CH_2—NHPh Cl^-(X)			4.99	1.51
o-Me_2N—C_6H_4—NHPh (VII)		6.56	7.42–7.63	0.86–1.07

[a] Measured in ppm downfield of internal Me_4Si in 10–15% solutions in $CDCl_3$ unless otherwise specified.
[b] In dimethyl sulphoxide-d_6 as solvent.

um salt was obtained from the amine (VII) by reaction with one mole of methyl *p*-toluenesulphonate (tosylate). Use of methyl iodide resulted in alkylation at both nitrogen atoms and the formation of complex mixtures.

A compound in which the arsenic atom is separated from the nitrogen atom by two saturated carbon atoms was also required and though the parent arsine was readily available, *e.g.* (VIII) and (IX), attempted alkylation invariably led to inseparable mixtures resulting from methylation at both arsenic and nitrogen. Prior

$$Ph_2AsLi + PhN\!\!\diagup\!\!\diagdown \longrightarrow Ph_2AsCH_2CH_2NHPh$$
(VIII)

$$o\text{-}BrC_6H_4CH_2Br + PhNH_2 \longrightarrow o\text{-}BrC_6H_4CH_2NHPh + (o\text{-}BrC_6H_4)_2NPh$$

$$\xrightarrow{(1)\ BuLi\ \downarrow\ (2)\ Ph_2AsCl}$$

$$o\text{-}Ph_2AsC_6H_4CH_2NHPh$$
(IX)

blocking of the NH group as the toluene-*p*-sulphonamide was unsuccessful as

TABLE 2

ULTRAVIOLET SPECTRA OF 5,10-DIHYDROPHENARSAZINES AND RELATED COMPOUNDS[a]

Compound	λ(nm)	log ε	Methiodide	
			λ(nm)	log ε
(I; X=Ph)	280	4.22	278	4.26
	310	4.07	308	4.09
	338	3.83	330	3.90
	284	4.08	275	4.19
(I; X=*o*-ClC_6H_4)	311	3.91	331	4.00
	280	4.08	270	4.20
(I; X=CH_3)	310	3.98	325	4.00
	276	3.74		
(I; X=Cl)[b]	306	4.06		
	357	4.36		
(V)	240	4.09	260	4.23
	320	3.52	330	3.49
(XI)	(211)	(4.53)	(215)	4.67
	240(sh)	4.09		
	300	4.40	315	4.44
	250	5.3		
Acridine[c]	355	4.0		
	256[d]	5.1		
	255[d]	4.2		
5,10-Dihydroacridine[c]	289	4.14		

[a] Solvent 95% ethanol. [b] Hexane solvent; from ref. 13. [c] From ref. 14. [d] In 0.5 *N* HCl; from ref. 15.

hydrolytic removal of the protecting group after quaternisation caused extensive decomposition. Attempts to prepare alternative systems also failed but a suitable arsonium salt was finally obtained, (X), by reaction of dimethylphenylarsine with *N*-(2-iodoethyl)aniline hydroiodide.

$$PhAsMe_2 + PhNHCH_2CH_2I \cdot HI \rightarrow Ph\overset{+}{A}s(Me)_2CH_2CH_2NHPhI^- \quad (X)$$

A *p*-aminoarsine was desirable to confirm that the effect was not solely due to the proximity of the arsonium and amino groups. (*p*-Aminophenyl)diphenylarsine was prepared by the reaction of phenylmagnesium bromide and (*p*-aminophenyl)-diiodoarsine hydroiodide and converted to (*p*-anilinophenyl)diphenylarsine (XI) with benzyne[12]. [*p*-(Diphenylamino)phenyl]diphenylarsine was also obtained in this reaction. Difficulty was again experienced in methylating the amino-arsine solely at the arsenic atom but this was eventually achieved by the use of slightly more than one mole of methyl iodide and allowing the reaction to proceed at room temperature for an extended period.

$$p\text{-}H_2NC_6H_4AsI_2 \cdot HI \xrightarrow{PhMgBr} p\text{-}H_2NC_6H_4AsPh_2 \xrightarrow[NaNH_2]{PhBr}$$

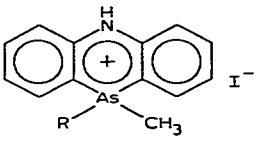
$$p\text{-}Ph_2NC_6H_4AsPh_2 + p\text{-}PhNHC_6H_4AsPh_2 \quad (XI)$$

The spectroscopic results are given in Tables 1 and 2.

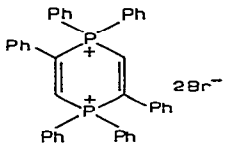
DISCUSSION

^1H NMR data

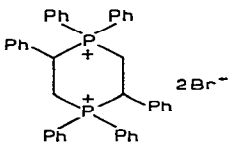
The data in Table 1 show that in the dihydrophenarsazines themselves, the magnitude of the downfield shift of the NH proton on quaternisation (4.12–4.23 ppm) is at a maximum and suggests the possibility of a pseudo-aromatic system which may be formally represented as (XII). Such a structure involves the lone pair of electrons on



(XII)



(XIII)



(XIV)

nitrogen and the empty *d* orbitals of arsenic. This is analogous in many respects to the structure proposed for the cyclophosphazines[16] which have been the subject of intensive study. The dihydrophenarsazine system differs fundamentally in that the atoms involved are not adjacent and any interaction will occur via mutual overlap of the hetero atom orbitals with the π-electron system of the aromatic rings. Though there seems to be no *a priori* objection to such a process, it apparently has not been reported previously. Aguiar has observed that in the bis salt (XIII) the chemical shift of the phosphorus atom is positive (with respect to phosphoric acid) instead of strongly negative as in the saturated analogue (XIV), and has interpreted this as being indicative of d_π–p_π bonding of the phosphorus atoms and the olefinic bonds[17].

A ring current of the type implied by the representation (XII) would, of course, account for the downfield shift of the NH proton [*cf.* pyrrolidine, δ(NH) 1.5–1.8, and pyrrole, δ(NH) 7.53], whereas a simple proximity effect should not be so large. Current theories concerning the structure of the cyclophosphazines fall into two groups, one of which suggests that conjugation is continuous around the ring[18] whereas the other envisages "islands of aromatic character" with conjugation interrupted at each phosphorus atom[19]. Though there is no definitive evidence in favour of one or the other, the bulk of the experimental results seems best interpreted by the island hypothesis.

Our results suggest that a similar "island" conjugation is operating in the phenarsazines, since the effect is observed when no system such as (XII) is possible. Thus, As methylation of the azarsepine (V) gives a downfield shift less than in the dihydrophenarsazines but still large. Similarly the *p*-aminoarsine (XI) shows a substantial downfield shift on alkylation, larger, in fact, than for the azarsepine. This cannot be accounted for in terms of deshielding by an adjacent arsonium centre. Interaction is occurring in both systems though a ring current is possible in neither.

If these shifts are due to a d_π–p_π interaction, then they will not be observed in systems where such overlap cannot occur and this is seen to be the case in the amine-ammonium salt (VI) and in the acyclic arsonium salt (X) where the downfield shifts are quite moderate.

Attempted extension of this study to the phenarsazine oxides was unsatisfactory since these compounds are insufficiently soluble in chloroform or dimethyl sulphoxide to give useful spectra. The oxides were soluble in methanol but solvent has a strong effect on the chemical shift of the NH proton in the arsines themselves, possibly due to hydrogen bonding. There is an appreciable but much smaller effect in the methiodides. Table 3 shows the effect of solvent on the arsine (I; X = *o*-ClC_6H_4) and its methiodide.

The chemical shift of the NH proton in the chloro compound (I; R = Cl) is of considerable interest. It could only be determined approximately since it was obscured by the absorption due to the aromatic protons, but it is clearly at appreciably lower field than in the compounds (I; X = alkyl or aryl). Such behaviour is in accord with the concept[20] that d_π–p_π orbital overlap is facilitated by electronegative substituents which serve to contract the *d* orbitals. Though the downfield shift (between 0.6 and 1.2 ppm) is slight by comparison with the arsonium salts, it is nevertheless considerably larger

TABLE 3

EFFECT OF SOLVENT ON CHEMICAL SHIFT (δ) OF NH PROTON IN 10-(*o*-CHLOROPHENYL)-5,10-DIHYDROPHENARSAZINE (I; X = *o*-ClC_6H_4) AND ITS METHIODIDE

Compound	Solvent		
	$CDCl_3$	dimethyl sulphoxide-d_6	Methanol
Arsine	6.21	9.33	8.40
Methiodide	10.43	10.76	10.33

than would be expected for any inductive effect of the chlorine atom. It is possible that d_π–p_π interaction accounts for the unexpected physical properties of the chloroarsine. It should be noted, however, that the yellow colour of this compound is not observed in the arsonium salts.

Ultraviolet spectra

Aryl-arsines, -arsonium salts, -arsonic and -arsinic acids, and -arsine oxides have been examined by this technique in recent years[21]. In general, trivalent compounds show evidence of strong interaction between the metal atom and the benzene rings which disappears entirely when this atom is alkylated or oxidised. This has been interpreted in terms of interaction involving the lone pair of electrons on arsenic and the π-orbitals of the benzene rings. Similarly, vinyl arsines show a band above 220 nm which is absent in the corresponding oxides[22]. The spectra of the oxides and arsonium salts are essentially the sum of the spectra expected of the individual aromatic systems, and there is no evidence of interaction between them via the arsenic atom.

Apart from some early work by Gibson and Johnson[23] the only results obtained with the dihydrophenarsazines are due to Mohler and his collaborators[13,24]. These authors found that the spectrum of the chloro compound (I; X = Cl) in hexane

was complex, in particular it showed two long wavelength (> 300 nm) bands of medium intensity which were completely absent from the spectrum of diphenylarsinous chloride. They interpreted this as evidence of interaction of the lone pairs of both heteroatoms with the benzene rings. Table 2 shows that the presence of these long wavelength bands is common to the dihydrophenarsazines, (I). Since neither diphenylamine nor 5,10-dihydroacridine show any such bands, it is reasonable to assign them to the ring system as a whole. By analogy with previous work[21] the bands might be thought to arise from overlap involving the lone pair of electrons on arsenic. In support of this the azarsepine (V) and the *p*-aminoarsine (XI) also show such bands. This interpretation is probably not correct, however, since alkylation of the arsenic does not remove the band from the spectrum of the resulting arsonium salt. Indeed, a bathochromic shift (10–20 nm) and a slight increase in intensity are usually observed. It is, of course, conceivable that the long wavelength bands present in the arsines and their corresponding arsonium salts arise from entirely different transitions, but this does not seem likely. Acridine itself shows a long wavelength band of similar intensity but this disappears in 5,10-dihydroacridine which has essentially a diphenylamine spectrum.

The overall spectral change in the dihydrophenarsazines on quaternisation is reminiscent of the changes observed in the spectra of nitrogen aromatics on protonation, *e.g.* quinoline[25], rather than any profound disruption of the absorbing system. The presence of the nitrogen atom is necessary for the appearance of the long wavelength band since no such absorption is present in the spectrum of 9-phenyl-9-arsafluorene[26].

These results are difficult to reconcile with the currently accepted theory[21], namely, that the spectral characteristics of trivalent arylarsenic compounds arise from interaction of the lone pair of electrons on arsenic with the π-electron systems of the aromatic rings. Recently it has been shown that the main band in triphenylarsine is unaffected by formation of a 1/1 charge transfer complex with iodine[27], implying that either the lone pair of electrons on arsenic is not involved in the formation of the complex or that this band does not arise from interactions involving the lone pair. Our results suggest that the same type of absorption is occurring in both the aminoarsines and their methiodides. If this is correct and the alternative explanation of d_π–p_π interaction is accepted, then *d* orbital overlap must be significant in the arsines as well as the salts. This is unexpected since it has been calculated[28] that the involvement of *d* orbitals should contribute little in, for example, pentaphenylarsole. The assumption of d_π interaction as a general explanation of the ultraviolet spectra of arylarsines does not, however, explain the effect of quaternisation on simple aryl arsines.

Instances of d_π–Ar_π interaction have been reported for trivalent phosphorus and other elements. Bissey and Goldwhite have obtained spectral evidence for electron withdrawal by phosphorus *d* orbitals in (*p*-methoxyphenyl)phosphine[29]. The acids p-$HO_2CC_6H_4MR_3$ (M = Si, Ge, Sn) are all stronger than the carbon analogue (M = C)[30]. Addition of nucleophiles to vinylphosphines occurs at the β-carbon atom, suggesting electron withdrawal by phosphorus[31]. Spectral and substituent effect studies by Schiemenz[32] also indicate that the Ph_2P group is electron withdrawing though Baldwin *et al.* found it to be effectively neutral[33].

The ultraviolet evidence strongly suggests that d_π–p_π interaction is extensive in

both arsines and arsonium salts, though more pronounced in the latter. The effect is no doubt enhanced in the dihydrophenarsazines by the ability of nitrogen to release electrons to the rings: the effect is, however, much more pronounced in these compounds than in related cases involving phosphorus such as [*p*-(dimethylamino)-phenyl]phosphonium salts[34] and phosphine oxides[35].

Electron withdrawal by *d* orbital overlap provides an alternative explanation of Mann's concept of "inductive deactivation"[36–38] and may also account for the stability of structures in which positively charged arsenic is linked to carbon by a formal double bond[8,9].

EXPERIMENTAL

All compounds are colourless unless otherwise noted. ^{1}H NMR spectra were measured in 10–15% solutions in $CDCl_3$ on Varian A-60 and HA-100 instruments. The identity of the NH protons was confirmed by D_2O exchange in each case. Molecular weights were determined by mass spectrometry on an AEI-MS9 instrument at Sydney University. Ultraviolet spectra were measured in 95% ethanol on a Perkin–Elmer 137. Melting points were determined on a Kofler hot stage and are uncorrected. Chromatography was carried out on alumina (Peter Spence, Grade H). Thin-layer chromatography (TLC) was performed on microscope slides dip coated with Kieselgel. Dry distilled solvents were used throughout. Petrol refers to the fraction b.p. 60–80° and ether refers to diethyl ether.

Dihydrophenarsazines were prepared by addition of the appropriate Grignard reagent (2 mols) to the chloro compound (I; X=Cl). The known compounds had physical and spectral properties in agreement with literature values. The characterisation of the 10-(2-chlorophenyl) compound and of the azarsepine (V) have been described elsewhere[39].

N,N-Dimethyl-N'-phenyl-o-phenylenediamine (VII)

Anhydrous K_2CO_3 (5.2 g, 2 mols), *N*-phenyl-*o*-phenylenediamine (3.5 g) and methyl iodide (40 g, 15 mols) in benzene (40 ml) were boiled under reflux in a nitrogen atmosphere and in the absence of light (28 h). The cooled mixture was filtered and the residue washed with benzene. The combined filtrate and washings were evaporated and the residual oil chromatographed over alumina (140 g). Elution with petrol/benzene (4/1) afforded the desired amine as an air-sensitive, pale yellow oil (2.5 g). ^{1}H NMR: δ 7.18, m, 9 H, ArH; 4.91; 6.56, s, 1 H, NH; 2.67, s, 6 H, NMe_2). It was converted to its acetamide for characterisation by treating first with butyllithium (1 mol) followed by acetyl bromide (1 mol). The mixture was stirred (0.5 h), hydrolysed with water, and made basic with Na_2CO_3. Ether extraction, evaporation and recrystallisation (ethanol) of the residue afforded the amide (60%), m.p. 67°. (Found: C, 75.8; H, 7.1; N, 10.9. $C_{16}H_{18}N_2O$ calcd.: C, 75.6; H, 7.1; N, 11.0%.) ^{1}H NMR: δ 7.25, m, 9 H, ArH; 2.70, s, 6 H, NMe_2; 2.09, s, 3 H, $COCH_3$. With pyridine/acetic anhydride as the acetylating agent no reaction occurred. Other attempts to prepare this amine were as follows: (*a*) Methylation with dimethyl phosphonate. This gave an oil (49%) whose ^{1}H NMR and infrared spectrum showed it to be the fully methylated compound. δ 6.93, m, 9 H, ArH; 3.10, s, 1 H, Ar_2NMe; 2.67, s, 6 H, NMe_2. (*b*) Reaction of the benzyne from *o*-chloro-*N,N*-dimethylaniline with aniline. Carrying out this

reaction according to Caubere[12] led to *N,N*-dimethyl-*N'*-phenyl-*m*-phenylenediamine (37%); presumably formation of the 2-isomer is sterically hindered[40].

(o-Anilinophenyl)trimethylammonium p-toluenesulphonate (VI)

The amine (0.7 g) and methyl-*p*-toluenesulphonate (0.61 g, 1 mol) were heated together (80°, 1 h) and the resulting solid afforded the salt on recrystallisation (methanol/ether), m.p. 191° (0.5 g, 38%). (Found: C, 65.9; H, 6.5; N, 6.6. $C_{22}H_{26}N_2O_3S$ calcd.: C, 66.3; H, 6.6; N, 7.0%.) This salt was converted to the iodide by shaking its solution in $CDCl_3$ with aqueous potassium iodide. The NH proton was located by observing a 1 proton decrease in the integral in the range δ 7.42–7.63 when the NH proton was exchanged with D_2O.

(2-Anilinoethyl)diphenylarsine (VIII)

A solution of lithium diphenylarsenide was prepared from triphenylarsine (7.68 g) and lithium (0.35 g; 2 mols) in tetrahydrofuran by the method of Aguiar and Archibald[41]. *N*-Phenylaziridine[42] (3 g) in ether was added dropwise (0.5 h) and the mixture refluxed (1.5 h), cooled, water (30 ml) added and the ether layer separated, dried, and evaporated giving an oil which was distilled, b.p./0.1 mm 200–206° (6.8 g). Chromatography on alumina and elution with petrol/benzene (7/3) removed first some residual triphenylarsine followed by pure (VIII) (5.8 g; 66%) as a colourless oil. (Found: C, 69.2; H, 6.1; N, 4.1. $C_{20}H_{20}AsN$ calcd.: C, 68.8; H, 5.7; N, 4.0%.) ^{1}H NMR: δ 7.28, m, 15 H, ArH; 3.48, s, 1 H, NH; 3.24, m, 2 H, CH_2N; 2.21, m, 2 H, CH_2As.

(2-Anilinoethyl)dimethylphenylarsonium iodide (X)

2-Anilinoethanol (40 g) was added dropwise to hydriodic acid (114 ml, 55%) at 0° followed by distillation to remove the water (65 ml). The residual crystalline mass was dried by suction filtration and washed repeatedly with ether, affording *N*-(2-iodoethyl)aniline hydroiodide (60 g, 55%), m.p. 118°. (Found: C, 25.8; H, 2.9; N, 4.1. $C_8H_{11}I_2N$ calcd.: C, 25.6; H, 2.9; N, 3.7%.) A solution of this salt (1.5 g; 1.1 mol) and dimethylphenylarsine (0.7 g) in ethanol (2 ml) was refluxed (4 days), ether added, and the precipitated gum separated and taken up in chloroform. This solution was washed successively with water, aqueous sodium carbonate (10%) and water, then dried and evaporated. The residual gum was recrystallised from chloroform/ethyl acetate to give (X) (0.21 g; 13%), m.p. 158°. (Found: C, 44.7; H, 4.8. $C_{16}H_{21}AsIN$ calcd.: C, 44.8; H, 4.9%.) ^{1}H NMR: δ 7.30, m, 10 H, ArH; 4.99, bs, 1 H, NH; 3.56, bm, CH_2CH_2; 2.45, s, 6 H, $AsMe_2$.

[(o-Anilinomethyl)phenyl]diphenylarsine (IX)

o-Bromobenzyl bromide (21.1 g), aniline (7.9 g) and anhydrous K_2CO_3 (11.7 g) were refluxed (4 h), cooled, filtered, and the residue washed with chloroform. The combined filtrate and washings were evaporated and the isoamyl alcohol removed by steam distillation. The residual oil was taken up in hot ethanol and on cooling deposited crystals of *N,N*-bis(*o*-bromobenzyl)aniline (1.4 g, 8%), m.p. 135°. (Found: C, 55.6; H, 4.3; N, 3.2. $C_{20}H_{17}Br_2N$ calcd.: C, 55.7; H, 3.9; N, 3.2%.) ^{1}H NMR: δ 7.20, m, 13 H, ArH; 4.67, s, 4 H, $(CH_2)_2N$.

The ethanol-soluble portion of the mixture was fractionally distilled. After a small forerun *N*-(*o*-bromobenzyl)aniline (7.2 g, 33%) passed over, b.p./0.2 mm

140–144°. It slowly crystallised on cooling, m.p. 42–44°. ^{1}H NMR: δ 7.11, m, 9 H, ArH; 4.35, s, 2 H, CH_2N; 4.23, s, 1 H, NH. The compound darkened rapidly on exposure to air and was converted into its benzamide (Schotten–Baumann) for characterisation, m.p. 98° (ethanol). (Found: C, 65.3; H, 4.5; N, 3.9. $C_{20}H_{16}BrNO$ calcd.: C, 65.6; H, 4.4; N, 3.8%.)

The amine (2.5 g) in ether (40 ml) was added to a solution of butyllithium (23.4 ml, 1.6 *M*, 4 mols) in petrol containing *N,N,N',N'*-tetramethylethylenediamine (4.4 g). The solution was stirred (1 h) and diphenylarsinous chloride (7.5 g; 3 mols) in ether (20 ml) was added dropwise. After further stirring (1 h) the mixture was hydrolysed and the organic layer separated, dried, and evaporated. Distillation of the residue (0.3 mm) afforded two fractions: (*a*) b.p. 120–150° and (*b*) b.p. 190–220°. Fraction (*a*) had a high aliphatic content (^{1}H NMR) and was discarded. Fraction (*b*) was chromatographed on alumina (170 g) and eluted with benzene/petrol (1/9), which removed material similar (TLC) to fraction (*a*). Elution with benzene then gave (IX) (1.1 g; 28%), m.p. 135°. (Found: mol.wt., 411.0978. $C_{25}H_{22}AsN$ calcd.: mol.wt., 411.0968.)

(p-Anilinophenyl)diphenylarsine (XI)

(*p*-Aminophenyl)arsonous diiodide hydroiodide (12 g) was added in small portions to a solution of phenylmagnesium bromide (69.2 g; 20 mols) in ether (300 ml), the mixture stirred (1 h) and hydrolysed with aqueous ammonium chloride. The ether layer was separated, concentrated to 100 ml and washed with aqueous hydrochloric acid (10%). Benzene was added to dissolve the oil which separated and the organic layer was removed, dried, and diluted with ether, precipitating (*p*-aminophenyl)-diphenylarsine hydrochloride (5.0 g; 64%), m.p. 127°, from methanol/ether. (Found: C, 60.4; H, 4.7; N, 4.1. $C_{18}H_{17}AsClN$ calcd.: C, 60.5; H, 4.8; N, 3.9%.) The free arsine was obtained as an oil by treating this salt with aqueous KOH. ^{1}H NMR: δ 7.25, m, 14 H, ArH; 3.53, s, 2 H, NH_2. It was converted to its acetyl derivative by pyridine/acetic anhydride (61%), m.p. 140° from aqueous ethanol. (Found: C, 66.1; H, 5.1; N, 4.0. $C_{20}H_{18}AsNO$ calcd.: C, 66.1; H, 5.0; N, 3.9%.)

Sodamide (0.24 g, 1.2 mols) was added to a solution of the arsine (2 g) in hexamethylphosphoric triamide (5 ml) and tetrahydrofuran (5 ml) and the mixture stirred under nitrogen (2 h). Bromobenzene (1 g, 1 mol) was added, followed by further sodamide (0.73 g, 3.6 mols) added portionwise during 2 h. The mixture was warmed to 45° and stirred (19 h), cooled, poured onto ice and extracted with benzene. The organic layer was washed with water, dried, evaporated, and the residue chromatographed on alumina (100 g). Petrol/benzene (9/1) eluted [*p*-(diphenylamino)phenyl]-diphenylarsine (0.45 g), m.p. 110°, from petrol. (Found: mol.wt., 473.1132. $C_{30}H_{24}AsN$ calcd.: mol.wt., 473.1124.) It formed a methiodide, m.p. 178° from methanol/ether. (Found: C, 60.7; H, 5.05. $C_{31}H_{27}AsIN$ calcd.: C, 60.5; H, 4.4%.)

Further elution of the column with benzene/petrol (3/7) gave (XI) (0.5 g; 20%) as pale yellow crystals, m.p. 69°. (Found: mol.wt., 397.0817. $C_{24}H_{20}AsN$ calcd.: mol.wt., 397.0811.) ν_{max} 3360 cm^{-1} (NH). ^{1}H NMR: δ 7.23, m, 19 H, ArH; 5.45, s, 1 H, NH. The methiodide was obtained (88%) by allowing the arsine (90 mg) and methyl iodide (42 g; 1.1 mol) in acetonitrile (2 ml) to stand at room temperature (13 days), m.p. 215°, from methanol/ether. (Found: C, 55.2; H, 4.4; N, 2.7. $C_{25}H_{23}AsIN$ calcd.: C, 55.6; H, 4.2; N, 2.6%.)

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