Synthesis of Some Nitrogen–Arsenic Heterocycles: 5,10-Dihydro-5,10-*o*-benzenophenarsazine (Azarsatriptycene), 10,11-Dihydro-5-phenyl-5*H*-dibenzo[*b*,*f*][1,4]azarsepine, and 2,3-Dihydro-1,2-diphenyl-1*H*-benz[*c*]-azarsole

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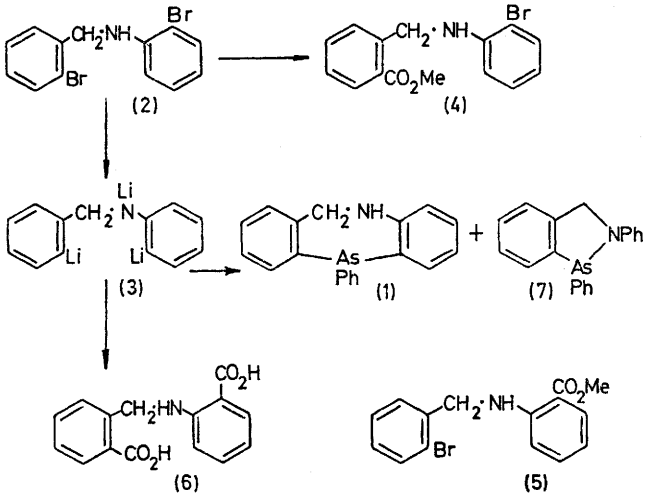
10,11-Dihydro-5-phenyl-5*H*-dibenzo[*b*,*f*][1,4]azarsepine (1) and 1,2-dihydro-1,2-diphenyl-1*H*-benz[*c*]azarsole (7) are formed in low yield in the reaction between *o*-lithio-*N*-(*o*-lithiobenzyl)aniline and dichloro(phenyl)arsine. Azarsatriptycene (12) is prepared by cyclising 10-(2-chlorophenyl)-5,10-dihydrophenarsazine with an excess of lithium diethylamide in ether. The triptycene is a neutral compound which resists quaternisation and is unaffected by acids and bases. The arsenic–carbon bond is cleaved by treatment with sodamide in hexamethylphosphoramide to give 5,5′,10,10′-tetrahydro-5,5′-diphenyl-10,10′-oxydiphenarsazine (10).

In connection with a spectroscopic study of phenarsazines we required an *o*-aminoarylarsine, preferably with both heteroatoms incorporated in a ring. The azarsepine (1) promised to be accessible from the reaction of the appropriate dilithio-compound with a dichloroarsine.

o-Bromo-*N*-(*o*-bromobenzyl)aniline (2) was prepared from *o*-bromobenzyl bromide and *o*-bromoaniline and its conversion into the lithio-compound (3) was studied by treating it with *NNN′N′*-tetramethylethylenediamine–n-butyl-lithium (1 : 1) and carboxylating the product. With 2·7 moles of this reagent only one of the bromine atoms was replaced, and 2-bromo-*N*-(2-carboxybenzyl)aniline (4; R = H) was obtained (53%). This was identified from the ^{1}H n.m.r. spectrum of the methyl ester (4; R = Me), which showed the NH signal as a broad singlet at δ 4·91 p.p.m. In the spectrum of the alternative isomer (5) the NH signal would

be expected at considerably lower field, owing to shielding by the adjacent methoxycarbonyl group. This was confirmed by the spectrum of the ester (5) obtained from



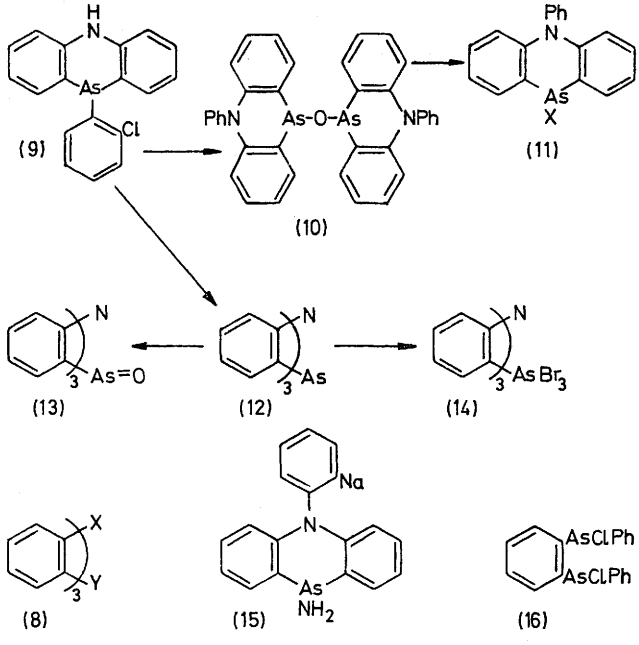
o-bromobenzyl bromide and methyl anthranilate [δ 8·24 p.p.m. (NH)].

Treatment of the dibromo-amine (2) with a large excess of the butyl-lithium–diamine mixture followed by carboxylation afforded the dicarboxylic acid (6) (87%). Addition to the lithio-compound (3) thus prepared of an excess of dichloro(phenyl)arsine resulted in the precipitation of a large amount of insoluble material. The soluble portion of the mixture furnished the crystalline azarsepine (1) (4·5%), m.p. 117°, after distillation and chromatography. This was identified by microanalysis and high resolution mass spectrometry and by its ^{1}H n.m.r. spectrum which shows the benzylic proton signals as an AB (J 15 Hz) quartet and the NH signal as a broad singlet. Coupling between NH and CH_2 is not observed, presumably because of rapid intermolecular exchange; the methiodide of this compound shows CH_2·NH as an ABX system ($J_{AX} \simeq J_{BX} = 5$ Hz; J_{AB} 16·5 Hz).

The insoluble material formed was thought to arise from condensation of the amine group (as the *N*-lithio-derivative) with the dichloroarsine to give polymeric material. It was therefore treated with ethanolic hydrogen chloride in the hope of breaking the arsenic–nitrogen bonds and improving the yield of the azarsepine (1). Chromatography of the soluble material obtained in this way afforded a low yield (3%) of a crystalline solid, m.p. 150°, isomeric (mass spectrum) with the azarsepine. This is assigned the benzazarsoline structure (7) on the basis of microanalysis and molecular weight. The ^{1}H n.m.r. spectrum showed the benzylic methylene signal as an AB quartet (J 14·8 Hz) and the i.r. spectrum showed no NH absorption.

We hoped to explore routes to a phosphine in which the phosphorus atom occupied a bridgehead position in order to be able to study the chemistry of phosphorus under conditions where the geometry of the substituents was fixed. One such structure would be a triptycene in which one or both of the bridgehead carbon atoms was replaced by phosphorus (8; X = P, Y = CH or P). A good starting point seemed to be the phenophosphazines, which are relatively easily accessible. We first examined the corresponding phenarsazines since these are easily prepared and their chemistry has been extensively studied.[1]

10-Chloro-5,10-dihydrophenarsazine reacts with *o*-chlorophenylmagnesium bromide to give the corresponding tertiary arsine (9) in good yield, contaminated with traces of the 2-bromophenyl compound. Attempts to cyclise this material under Ullmann conditions were unsuccessful and we turned our attention to the generation of a benzyne which could cyclise on to the nitrogen atom. Wittig and Steinhoff [2] have successfully used this method to prepare the azatriptycene (8; X = N, Y = CH) from 10-(2-chlorophenyl)-5,10-dihydroacridine and potassium amide in liquid ammonia. The recently developed method of Caubere,[3] using sodamide in hexamethylphosphoramide–tetrahydrofuran is more convenient; treatment of the arsine (9) with a large excess of sodamide in this solvent converted it in good (70%) yield into a new crystalline material, m.p.



253°. The mass spectrum of this product, however, indicated the molecular weight to be 652 and high resolution mass matching showed the molecular formula to be $C_{36}H_{26}As_2N_2O$. The i.r. spectrum showed no NH absorption and the product was hence assigned the structure 5,5′,10,10′-tetrahydro-5,5′-diphenyl-10,10′-oxydiphenarsazine (10). The structure is confirmed by the following facts: recrystallisation from ethanol

[1] F. G. Mann, ' The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, Bismuth, and Silicon,' Interscience, New York, 1950, p. 80.

[2] G. Wittig and G. Steinhoff, *Annalen*, 1964, **676**, 21.

[3] P. Caubere, *Bull. Soc. chim. France*, 1967, 3446.

affords 10-ethoxy-5,10-dihydro-5-phenylphenarsazine, m.p. 144° (11; X = OEt), and this is converted by methylmagnesium iodide into the methyl arsine (11; X = Me), m.p. 114°. An authentic sample of this was prepared from 5,10-dihydro-10-methylphenarsazine and bromobenzene by reaction with sodamide in hexamethylphosphoramide. The methiodide of this arsine was identical (m.p. and mixed m.p., u.v., and ^{1}H n.m.r. spectra) with that obtained from the arsine prepared *via* the oxydiphenarsazine (10).

In addition to the principal product, this attempted preparation of the azarsatriptycene (12) also yielded small amounts of triphenylamine and biphenyl, the formation of which is obscure. A further product of unknown origin is 5,10-dihydro-10-phenylphenarsazine (9; Ph for *o*-ClC_6H_4); Wittig and Steinhoff [2] isolated a small amount of 5,10-dihydro-10-phenylacridine in their preparation of azatriptycene.

Treatment of the oxydiphenarsazine (10) with hydrochloric acid converts it into the chloroarsine (11; X = Cl). Such arsines customarily cyclise readily in the phenarsazine series, and diarsatriptycene (8; X = Y = As) has been prepared in this way by simply heating the bis(chloroarsine) (16).[4] However, the chloroarsine (11; X = Cl) was unchanged after vacuum sublimation or heating at 200° for 6 hr. at atmospheric pressure.

The azarsatriptycene (12) was ultimately obtained (48%) by cyclising the 2-chlorophenylarsine (9) with lithium diethylamide in ether. The product has the high m.p. (233°) and ease of sublimation expected. The u.v. spectrum is similar to that of azatriptycene and that of triptycene itself [2] in that no evidence for interaction of the heteroatoms and the aromatic rings is present, and only weak absorption occurs above 220 nm. It differs from them, however, in showing no resolved fine structure in the 265—280 nm. region, where two weak bands can be seen for both azatriptycene and triptycene. The mass (M^+ 317) and i.r. (no NH band) spectra further confirm the structure.

The outstanding feature of the chemistry of azarsatriptycene is its lack of reactivity. Whereas Sasse and Jackson [5] have shown that Raney nickel quantitatively cleaves triphenyl-phosphine or -arsine to benzene, the triptycene (12) gives only a 31% yield of triphenylamine, and 50% of the starting material is recovered. In contrast to the azatriptycene the azarsa-analogue is insoluble in hydrochloric or hydrobromic acid in the cold, and though it dissolves when heated it separates unchanged when the solution is cooled. It is unaffected by boiling (3 hr.) with 48% aqueous hydrogen bromide or 48% hydrogen bromide in acetic acid, though this treatment normally cleaves arylarsines.[6] Boiling with concentrated nitric acid converts it into the oxide (13) (95%) without appreciable nitration, in marked contrast to ready reaction of either triarylamines [7] or triarylarsines [8] with this reagent. The absence of basic character is the more unexpected since the azatriptycene (8; X = N, Y = CH) is considerably more basic than triarylamines,[2] as would be expected in view of the absence of delocalisation of the lone pair of electrons on nitrogen in the azatriptycene.

Neither the arsenic nor the nitrogen atom in the azarsatriptycene is alkylated by boiling with methyl iodide, or by treatment with methyl iodide–silver fluoroborate [2] or triethyloxonium fluoroborate in the cold. When heated with methyl toluene-*p*-sulphonate at 180° for 4 hr., conditions under which the diarsatriptycene (8; X = Y = As) forms a monomethotoluene-*p*-sulphonate,[9] a black tar resulted but no salt could be detected. On the other hand, azarsatriptycene reacted readily in the cold with bromine in chloroform to give a very unstable, orange, crystalline compound (14) which when heated reverted to starting materials but on hydrolysis afforded the oxide (13). The structure of this bromide is obscure since it contains three bromine atoms per molecule. The triptycene (12) also reacts readily with potassium tetrachloropalladate(II) to give a bright yellow, apparently monomeric, complex, $(C_{18}H_{12}AsN)_2PdCl_2$, in which the arsenic atom is presumably co-ordinated to the palladium.

This lack of reactivity in the azarsatriptycene is similar to the behaviour of the diarsa-analogue (8; X = Y = As), though the latter compound forms a stable tetrabromide [4] and a monoquaternary salt has been prepared.[9] This behaviour may be steric in origin and arise from the considerable difference between the arsenic–carbon (1·95 Å) and nitrogen–carbon (1·54 Å) bond lengths. The shorter length of the C–N bond should tend to close the C–As–C angle and conversely the angle C–N–C should be somewhat flattened. The combined effect should be to distort the geometry at both atoms further from the tetrahedral situation in which both normally exist when quaternised or protonated. Thus either process should be more difficult for the triptycene (12) than for related but non-rigid systems. An *X*-ray study of the azarsatriptycene has been undertaken.

Though generally unreactive, azarsatriptycene reacts readily with sodamide in hexamethylphosphoramide–tetrahydrofuran, giving the oxydiphenarsazine (10) (85%), confirming the supposition that the triptycene (12) is an intermediate in the production of this compound from the 2-chlorophenylarsine (9) under the same conditions. The reaction presumably involves attack by amide ion at arsenic with the formation of the metallated aminoarsine (15), which on aqueous work-up would be expected to give the oxy-compound (10) by analogy with the hydrolysis of other aminoarsines.[10] The deep red colour of the mixtures leading to the oxydiphenarsazine suggested the presence of arsenide ions;

[4] N. P. McCleland and J. B. Whitworth, *J. Chem. Soc.*, 1927, 2753.
[5] G. D. Jackson and W. H. Sasse, *J. Chem. Soc.*, 1962, 3746.
[6] W. R. Cullen, *Adv. Organometallic Chem.*, 1966, **4**, 145.
[7] H. Ryan and M. Markey, *Proc. Roy. Irish Acad.*, 1926, **37***B*, 71.
[8] A. Michaelis, *Annalen*, 1902, **321**, 180.
[9] F. G. Mann and F. C. Baker, *J. Chem. Soc.*, 1952, 4142.
[10] V. Ipatiew, G. Rasuwajew, and G. Stromski, *Ber.*, 1929, **62***B*, 598.

however, treatment with methyl iodide prior to hydrolysis did not affect the yield of the oxy-compound (10). In this reaction no biphenyl or 5,10-dihydro-10-phenylphenarsazine were found but instead the principal minor product appeared to be 5,10-dihydro-5-methyl-10-phenylphenarsazine contaminated with an unknown high molecular weight compound. There appear to be no reported reactions analogous to the arsenic–carbon bond cleavage, though *N*-phenylpiperidine is formed by the action of sodamide and piperidine on phenylarsonic acid.[11]

The triptycene (12) was unchanged after 3 days under reflux with an excess of sodium ethoxide in ethanol.

EXPERIMENTAL

Petroleum refers to the fraction b.p. 60—80°. ^{1}H N.m.r. spectra were run for solutions in deuteriochloroform with Varian A60 or HA100 instruments; chemical shifts are quoted in p.p.m. (δ) downfield of internal tetramethylsilane and coupling constants are in Hz. I.r. spectra were recorded for Nujol mulls with a Perkin-Elmer Infracord, and u.v. spectra for solutions in 95% ethanol with a Perkin-Elmer 137UV instrument. Mass spectra were recorded with an A.E.I. MS9 instrument at Sydney University. Gas chromatography (g.l.c.) was carried out with a Perkin-Elmer 800 with a flame ionisation detector [6 ft. × ¼ in. column packed with SE30 (5%) on Chromosorb G]. M.p.s were determined with a Kofler hot-stage apparatus. Solvents were distilled before use; tetrahydrofuran was refluxed over lithium aluminium hydride and distilled immediately before use; solutions were dried with anhydrous sodium sulphate. Chromatography was carried out with Spence grade H alumina or B.D.H. silica gel. T.l.c. was carried out with microscope slides dip-coated with Kieselgel. All reactions involving use of organolithium reagents were performed under dry oxygen-free nitrogen. Compounds marked with an asterisk (*) were identified by comparison with authentic samples; at least two of the following criteria were used: m.p. and mixed m.p., u.v., i.r., ^{1}H n.m.r., and mass spectroscopy, t.l.c., and g.l.c.

o-*Bromo*-N-(o-*bromobenzyl*)*aniline* (2).—Anhydrous potassium carbonate (12·6 g.), *o*-bromobenzyl bromide (23·4 g.), and *o*-bromoaniline (16·1 g., 1 mol.) in isopentyl alcohol containing a trace of copper powder were boiled under reflux (16 hr.), and the alcohol was removed by steam distillation. The residue was extracted with chloroform and the extract was washed with water, dried, and evaporated. Recrystallisation from ethanol afforded o-*bromo*-N-(o-*bromobenzyl*)*aniline* (2), m.p. 67° (18 g., 67%) (Found: C, 45·7; H, 3·4; N, 3·8. $C_{13}H_{11}NBr_2$ requires C, 45·8; H, 3·2; N, 4·1%).

Lithiation.—n-Butyl-lithium in petroleum (1·7M; 4·7 ml., 2·7 mol.) was added to a solution of the benzylaniline (1 g., 1 mol.) in ether (10 ml.) containing *NNN'N'*-tetramethylethylenediamine (0·91 g., 2·7 mol.) and the solution was stirred (10 min.) and poured on solid carbon dioxide. Water was added and the solution was extracted with ether; the extract was washed with aqueous sodium hydrogen carbonate. Acidification of the hydrogen carbonate extract was followed by extraction with ether; drying and evaporation of this extract gave *o*-bromo-*N*-(*o*-carboxybenzyl)aniline, m.p. 151° (from ethanol) (0·42 g., 53%) (Found: C, 55·0; H, 4·2; N, 4·6%; equiv. wt. 280. $C_{14}H_{12}BrNO_2$ requires C, 54·95; H, 3·9; N, 4·6%; equiv. wt. 286). Ethereal diazomethane converted the acid into the methyl ester (4), m.p. 71° (from ethanol), δ 7·37 (8H, m, aromatic), 1·97 (1H, s, NH), 4·75 (2H, s, CH_2), and 3·90 (3H, s, CO_2Me).

Increasing the amount of butyl-lithium–diamine mixture to 5·7 mol. with the work-up as before, yielded, from the benzylaniline (1 g.) after 30 min. at room temperature, o-*carboxy*-N-(o-*carboxybenzyl*)*aniline* (6), m.p. 208° (from ethanol) (0·69 g., 87%) (Found: equiv. wt. 147. $C_{16}H_{15}NO_4$ requires equiv. wt. 135·5). It was converted into the *methyl ester*, m.p. 104° (from ethanol) (Found: C, 68·2; H, 5·8; N, 4·8. $C_{17}H_{17}NO_4$ requires C, 68·25; H, 5·7; N, 4·7%), δ 7·39 (9H, m, aromatic and NH), 4·83 (2H, s, CH_2), 3·89 (3H, s, CO_2Me), and 3·83 (3H, s, CO_2Me).

Methyl N-(o-*Bromobenzyl*)*anthranilate* (5).—The procedure was the same as for *o*-bromo-*N*-(*o*-bromobenzyl)-aniline, with methyl anthranilate used in place of *o*-bromoaniline. The *product* (64%) had m.p. 130° (from ethanol) (Found: C, 56·5; H, 4·45; N, 4·3. $C_{15}H_{14}BrNO_2$ requires C, 56·3; H, 4·4; N, 4·4%), δ 8·24 (1H, s, NH), 7·30 (8H, m, aromatic), 4·52 (d, *J* 6, CH_2), and 3·86 (3H, s, CO_2Me).

Reaction of the Lithio-compound with Dichloro(phenyl)-arsine.—*o*-Bromo-*N*-(*o*-bromobenzyl)aniline (7 g.) in anhydrous ether (100 ml.) was added dropwise to a solution of butyl-lithium (1·7M; 70 ml., 5·8 mol.) in petroleum containing the chelating diamine (14·4 g., 5·8 mol.). The mixture was stirred (30 min.), and dichloro(phenyl)arsine (12·5 g., 2·9 mol.) in dry ether (40 ml.) was added dropwise. A dense precipitate formed. The mixture was stirred (1 hr.), water (150 ml.) was added, and the organic layer was decanted, washed with water, dried, and evaporated, giving a brown oil (12 g.). Trituration of this with ether afforded oxo(phenyl)arsine * and distillation of the ether-soluble products at 0·3 mm. afforded three fractions, b.p. (*a*) 68—80° (2·3 g.), (*b*) 80—120° (0·9 g.), and (*c*) 180—210° (3·1 g.). Fraction (*a*) showed a high aliphatic–aromatic proton ratio in the ^{1}H n.m.r. spectrum, presumably due to dibutylphenylarsine, and was discarded. Fraction (*b*) was a complex mixture (t.l.c.) and was not further investigated. Fraction (*c*) contained three products (t.l.c.); chromatography on alumina (100 g.) and elution with benzene–petroleum (7 : 3) gave 10,11-*dihydro*-5-*phenyldibenzo*[b,f]-[1,4]*azarsepine* (1) (second component eluted), m.p. 117° (from ethanol) (0·4 g., 4·5%) (Found: C, 67·7; H, 5·11; N, 4·2%; *M*, 333·0492 ± 0·0007. $C_{19}H_{16}AsN$ requires C, 68·5; H, 4·8; N, 4·3%; *M*, 333·0498), $\nu_{max.}$ 3320 cm.$^{-1}$ (NH), $\lambda_{max.}$ 221 (log ε 4·45), 240sh (4·21), and 320 (3·52) nm. Boiling with methyl iodide in benzene gave the methiodide (45%), m.p. 132° (from methanol–ether). This compound gave unaccountably high carbon analyses and insufficient material was available for extensive purification. The ^{1}H n.m.r. spectrum was in accord with the structure and showed that *N*-methylation had not occurred (see text).

The ether-insoluble material obtained in this preparation was refluxed with ethanol–conc. hydrochloric acid (1 : 1). The mixture was evaporated and the residue was digested with chloroform–ethanol (1 : 1) and filtered. The insoluble material (1 g.) was tetramethylethylenediamine dihydrochloride.* The filtrate was evaporated and extracted with benzene and the benzene-soluble products (1·3 g.)

[11] T. K. Brotherton and J. F. Bunnett, *Chem. and Ind.*, 1957, 80.

were chromatographed on alumina (50 g.) and eluted with petroleum–benzene (1 : 1), affording in the first fraction 1,2-*dihydro*-1,2-*diphenyl*-1*H*-*benz*[c]*azarsole* (7) (0·26 g., 3%), m.p. 150° (from ethanol) (Found: C, 68·1; H, 4·7; N, 4·0%; *M*, 333. $C_{19}H_{16}AsN$ requires C, 68·5; H, 4·8; N, 4·2%; *M*, 333). Further elution gave mixtures of at least seven components (t.l.c.).

10-(2-*Chlorophenyl*)-5,10-*dihydrophenarsazine* (9).—10-Chloro-5,10-dihydrophenarsazine (30 g.), m.p. 192°, prepared from trichloroarsine and diphenylamine,[12] was added in portions to a solution of *o*-chlorophenylmagnesium bromide [13] (47·5 g., 2 mol.) in anhydrous ether (90 ml.). The solution was then boiled under reflux (15 min.) and hydrolysed with aqueous ammonium chloride; the ether layer was separated, dried, and evaporated, giving the *product* (29 g., 76%), m.p. 110° (from ethanol). The mass spectrum showed weak peaks at *m/e* 397 and 399, suggesting the presence of the 2-bromo-isomer arising from 2-bromophenylmagnesium chloride formed in the preparation of the Grignard reagent. The impurity could not be removed by repeated recrystallisation and gave rise to low carbon figures on analysis (Found: C, 60·4; H, 3·6; N, 4·2. $C_{18}H_{13}AsClN$ requires C, 61·1; H, 3·7; N, 4·0%). The *methiodide*, m.p. 136° (71%), similarly could not be purified by recrystallisation (Found: C, 45·2; H, 3·6; N, 3·1. $C_{19}H_{16}AsClIN$ requires C, 46·0; H, 3·2; N, 2·8%). Conversion to the oxide,[14] however, gave a derivative for which satisfactory analytical figures were obtained. The arsine (0·5 g.) in ethanol was diluted with water to the cloud point and a slight excess of ethanolic iodine solution (0·1M) was added. The solution was neutralised with sodium hydroxide (0·1M) and filtered; the precipitate was dried and yielded 10-(2-)*chlorophenyl*-5,10-*dihydro*-10-*oxophenarsazine*, m.p. 294—298° (decomp.) (from aqueous methanol) (0·3 g., 58%) (Found: C, 58·1; H, 3·7; N, 3·5. $C_{18}H_{13}AsClNO$ requires C, 58·5; H, 3·5; N, 3·8%).

Attempted Cyclisation of 10-(2-*Chlorophenyl*)-5,10-*dihydrophenarsazine with Sodamide*.—Sodamide (0·55 g., 1 mol.) was added to a solution of the phenarsazine (5 g.) in hexamethylphosphoramide (25 ml.) and tetrahydrofuran (10 ml.), and the mixture was stirred under nitrogen (2 hr.) while further sodamide (1·65 g., 3 mol.; when only a total of 2 mol. of amide were used starting material was recovered in high yield) was added in portions. Tetrahydrofuran (10 ml.) was then added and stirring was continued at 45° (65 hr.). The dark red solution was poured on ice, acidified with hydrochloric acid (2M), and extracted with chloroform; the extract was washed with water, dried, and evaporated. The resultant brown gum (4·9 g.) was chromatographed over alumina (200 g.) and eluted with benzene–petroleum (1 : 4), giving successively (*a*) a mixture of biphenyl * and triphenylamine * (0·086 g.; 5 : 2 ratio), (*b*) 5,10-dihydro-10-phenylphenarsazine * (0·12 g.), and (*c*) 5,5′,10,10′-*tetrahydro*-5,5′-*diphenyl*-10,10′-*oxydiphenarsazine* (10) (3·25 g., 70%), m.p. 253° (Found: C, 66·4; H, 4·0; N, 4·3%; *M*, 652·0481 ± 0·0012. $C_{36}H_{26}As_2N_2O$ requires C, 65·5; H, 4·1; N, 4·1%; *M*, 652·0476).

Repetition of the experiment with addition of methyl iodide (4·15 g., 1 mol.) in tetrahydrofuran (15 ml.) immediately before hydrolysis resulted in change of the red colour to yellow. Work-up and chromatography afforded the oxydiphenarsazine * (75%) and a faster-running material which contained (t.l.c.) at least four components, none of which corresponded to biphenyl. The major component was isolated by preparative t.l.c. (0·16 g.), m.p. 102—105° (from ethanol), δ 7·13 (13H, m, aromatic) and 3·34 (two almost coincident singlets, 2·7H, NMe). A sample of 5-*methyl*-10-*phenyl*-5,10-*dihydrophenarsazine*, m.p. 140°, obtained from 10-phenyl-5,10-dihydrophenarsazine by the method described later for the 5-phenyl-10-methyl analogue (50% yield) (Found: C, 68·2; H, 4·9; N, 4·6. $C_{19}H_{16}AsN$ requires C, 68·45; H, 4·8; N, 4·2%) showed δ 7·12 (13H, m, ArH) and 3·33 (3H, s, NMe).

The mass spectrum of the product, m.p. 102—105°, showed a peak at 333 corresponding to the methylphenyldihydrophenarsazine and also a peak at 648. The material appears to be a mixture of the methyl phenyl compound and a substance of a dimeric nature also containing an *N*-methyl group.

Recrystallisation of the oxydiphenarsazine from ethanol transformed it into 10-*ethoxy*-5,10-*dihydro*-5-*phenylphenarsazine* (11; X = OEt), m.p. 144° (Found: C, 66·35; H, 5·0; N, 3·6%; *M*, 363. $C_{20}H_{18}AsNO$ requires C, 66·15; H, 5·0; N, 3·9%; *M*, 363), δ 7·30 (13H, m, aromatic), 3·27 (2H, q, *J* 7, $O{\cdot}CH_2$), and 0·95 (3H, t, *J* 7, $CH_2{\cdot}CH_3$). The ethoxy-compound may be converted back into the oxy-compound (10) by dissolution in boiling ethyl acetate and reducing the volume to one third. The oxy-compound crystallises on cooling.

When the oxydiphenarsazine (10) (0·34 g.) is suspended in acetone (10 ml.) and hydrochloric acid (10M) is added dropwise, 10-*chloro*-5,10-*dihydro*-5-*phenylphenarsazine* (11; X = Cl) is precipitated (0·26 g.; 70%), m.p. 178° (from carbon tetrachloride) (Found: C, 61·0; H, 3·95; N, 3·95. $C_{18}H_{13}AsClN$ requires C, 61·2; H, 3·7; N, 4·0%).

5,10-*Dihydro*-10-*methyl*-5-*phenylphenarsazine* (11; X = Me).—(a) *From the ethoxy-compound* (11; X = OEt). The ethoxy-compound (0·27 g.) was added to a solution of methylmagnesium iodide (0·62 g., 5 mol.) in dry ether (10 ml.) and the mixture was refluxed (1 hr.), cooled, and hydrolysed with aqueous ammonium chloride. The ether layer was separated, dried, and evaporated, to give the *phenarsazine* (11; X = Me), m.p. 114° (from ethanol) (0·13 g., 50%) (Found: C, 68·4; H, 4·9; N, 4·4. $C_{19}H_{16}AsN$ requires C, 68·45; H, 4·8; N, 4·2%). Heating the arsine with methyl iodide gave a methiodide identical (m.p., mixed m.p., ^1H n.m.r., and u.v.) with the compound obtained in (b).

(b) *From* 5,10-*dihydro*-10-*methylphenarsazine*. Sodamide (0·1 g.) was added to a solution of 5,10-dihydro-10-methylphenarsazine [15] (0·4 g.) in hexamethylphosphoramide (4 ml.) and tetrahydrofuran (2 ml.). The solution was stirred (2 hr.) under nitrogen, and bromobenzene (0·32 g.) added, followed by sodamide (0·3 g.) added in portions during a further 2 hr. The mixture was stirred at room temperature (18 hr.), poured on ice, and extracted with ether, and the extract was dried and evaporated. The crude product was chromatographed over alumina (16 g.) and eluted with benzene–petroleum (1 : 4), giving material which was converted directly into its methiodide (0·22 g., 31% overall), m.p. 245—246° (from methanol–ether) (Found: C, 50·55; H, 4·3; N, 3·1. $C_{20}H_{19}AsIN$ requires C, 50·9; H, 4·0; N, 2·9%), δ 8·53 (2H, m, aromatic), 7·42 (9H, m, aromatic), 6·57 (2H, m, aromatic), and 2·95 (6H, s, AsMe).

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5,10-*Dihydro*-5,10-o-*benzenophenarsazine* (*Azarsatriptycene*) (12).—n-Butyl-lithium in petroleum (1·6M; 81 ml., 3 mol.) was added to a solution of 10-(2-chlorophenyl)-5,10-dihydrophenarsazine (15 g.) and diethylamine (9·4 g., 3 mol.) in dry ether (750 ml.); the mixture was boiled under reflux (5 days), water was added, and the ethereal layer was separated, dried, and distilled, leaving a residue which on recrystallisation (ethanol) afforded the *azarsatriptycene* (6·5 g., 48%), m.p. 233° [Found (for sublimed sample): C, 67·9; H, 3·9; N, 4·7%; *M*, 317. $C_{18}H_{12}AsN$ requires C, 68·2; H, 3·8; N, 4·4%; *M*, 317), $\lambda_{max.}$ 218 (log ε 4·59). No other distinct peak was observable but at 270 nm. the extinction coefficient was *ca.* 3000. When the triptycene (0·2 g.) and nitric acid (15M; 3 ml.) were boiled together (45 min.) 5,10-*dihydro*-10-*oxo*-5,10-o-*benzenophenarsazine* (13; 0·2 g.; 95%) was formed, m.p. 284—285° (from aqueous ethanol) (Found: C, 64·9; H, 3·9; N, 4·1%; *M*, 333. $C_{18}H_{12}AsNO$ requires C, 64·9; H, 3·6; N, 4·2%; *M*, 333).

A solution of the azarsatriptycene (0·2 g.) in dry chloroform was treated with a slight excess of bromine and diluted with dry ether, precipitating the *bromide* as orange crystals (0·3 g.). The product was washed thoroughly with ether and dissolved in dilute aqueous nitric acid; the bromine was estimated as silver bromide (Found: Br, 42·8. $C_{18}H_{12}AsBr_3N$ requires Br, 43·1%). The compound smelt of bromine and was decolourised when stored in a desiccator. Attempted determination of the m.p. regenerated the triptycene; * the orange colour disappeared at *ca.* 180°. Addition to aqueous alkali or aqueous ethanol afforded the triptycene oxide.*

Addition of potassium tetrachloropalladate(II) in aqueous ethanol to a solution of the triptycene (3 mol.) in hot ethanol precipitated the bright yellow *complex*, m.p. 305—310° (decomp.; darkened above 280°) (from chloroform) (Found: C, 52·2; H, 2·9; N, 3·0. $C_{36}H_{24}As_2Cl_2N_2$-Pd,H_2O requires C, 52·05; H, 3·1; N, 3·4%).

Reaction of Azarsatriptycene with Sodamide.—A solution of the triptycene (0·8 g.) in hexamethylphosphoramide (5 ml.) and tetrahydrofuran (2 ml.) was stirred with sodamide (0·2 g., 2 mol.) at 45° under nitrogen (24 hr.). At the end of this time no triptycene remained (t.l.c.), and work-up as described for the reaction of the 2-chlorophenylarsine furnished the oxydiphenarsazine * (0·7 g., 85%).

Reaction of the Azarsatriptycene with Raney Nickel.—The triptycene (0·5 g.) in methanol (100 ml.) was boiled under reflux with a large excess of methanol-washed Raney nickel (2 hr.), cooled, filtered, and evaporated. Preparative t.l.c. of the residue [Merck silica gel H, 9 × 9 in. plates, benzene–petroleum (1 : 1) as eluant] gave triphenylamine * (0·12 g., 31%) and starting material * (0·25 g., 50%) as the only two products.

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