Synthesis, Separation into Diastereoisomers, and Resolution of *o*-Phenylenebis(methylphenylarsine) and Related Studies of the *o*-Phenylenediarsine Moiety

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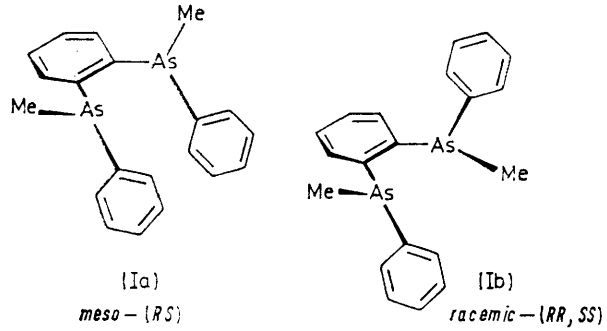
The nucleophilic substitution of *o*-dichlorobenzene by sodium methylphenylarsenide is described. The principal products of the reaction are *meso*- and *racemic*-*o*-phenylenebis(methylphenylarsine), although small quantities of the following compounds are formed as side-products: dimethylphenylarsine; ethoxymethylphenylarsine; methyldiphenylarsine; 1-chloro-2-methylphenylarsinobenzene; methylphenylarsinic acid; 1,2-dimethyl-1,2-diphenyldiarsane; 1,3-dimethyl-1,2,3-triphenyltriarsane; and 5,10-dihydro-5,10-diphenylarsanthren. A study of the possible stereospecific synthesis of *racemic*-*o*-phenylenebis(methylphenylarsine) from certain *o*-phenylenediarsine derivatives is described. The solid-state elimination of bromomethane from *o*-phenylenebis(dibromodimethylarsine) is stereospecific. The two diastereoisomers of *o*-phenylenebis(methylphenylarsine) have been separated and identified by means of their *fac*-[$PtMe_3(I)$(diarsine)] complexes using ^1H n.m.r. spectroscopy and the *racemic*-diarsine subsequently resolved *via* its D(−)-dibenzoylhydrogentartrate salt.

THE synthesis and study of the properties of asymmetric tertiary arsines and phosphines is of interest in connection with the geometrical and optical properties of their metal complexes, and also because of the potential offered by the optically active complex species in promoting stereospecific catalysis of reactions of suitable substrate molecules.[1]

The formation of metal complexes is particularly important in enhancing the physical differences between diastereoisomeric chelating agents, especially where a large degree of free rotation is possible in the uncoordinated ligand.[2] Earlier work includes an important article by Bercz and Horner [3] on the separation of the stereoisomers of *trans*-bis[1,2-bis(methylphenylphosphino)ethane]dichlororuthenium(II) complexes. Use has also been made of this stabilising effect in separating the diastereoisomers of 1,2-bis(methylphenylarsino)-ethane by column chromatography of the isomeric dichloropalladium complexes.[4]

The identification of the separated diastereoisomers presents an additional practical problem. Two basic approaches are employed in this respect: first, attempted resolution of the diastereoisomers as their quarternary salts with an optically active anion;[4] and secondly, careful design of suitable metal complexes which allow ready distinction of the diastereoisomeric metal complexes to be made on the basis of a direct physical measurement, *e.g.* ^{13}C n.m.r. spectroscopy [1] and *X*-ray



(Ia) *meso* − (*RS*) (Ib) *racemic* − (*RR*, *SS*)

analysis.[5] The latter approach was also employed by Cheney and Shaw [6] where p.m.r. spectroscopy was used to differentiate between the iodotrimethylplatinum(IV) complexes of *meso*- and *racemic*-1,2-bis(methylphenylarsino)ethane. Similarly, Cullen and Mihichuk *et al.*[7]

[1] K. Henrick and S. B. Wild, *J.C.S. Dalton*, 1974, 2500.
[2] B. Bosnich, W. G. Jackson, and S. B. Wild, *J. Amer. Chem. Soc.*, 1973, **95**, 8269; *Inorg. Chem.*, 1974, **13**, 1121.
[3] J. P. Bercz and L. Horner, *Annalen*, 1967, **703**, 17.
[4] B. Bosnich and S. B. Wild, *J. Amer. Chem. Soc.*, 1970, **92**, 459.
[5] J. C. Dewan, K. Henrick, D. L. Kepert, K. R. Trigwell, A. H. White, and S. B. Wild, *J.C.S. Dalton*, 1975, 546.
[6] A. J. Cheney and B. L. Shaw, *J. Chem. Soc.* (*A*), 1971, 3545, 3549.
[7] W. R. Cullen and L. Mihichuk, *Canad. J. Chem.*, 1973, **51**, 936.

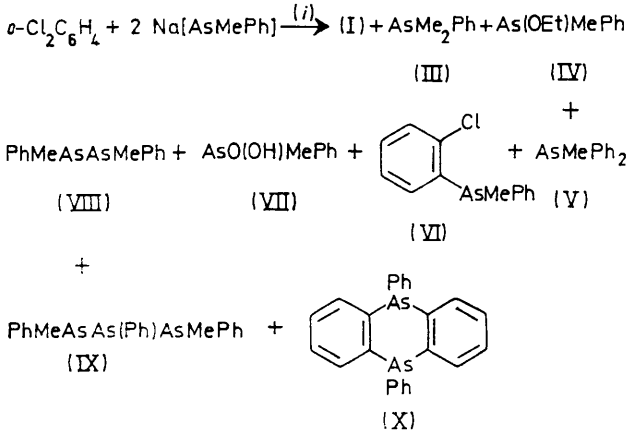
identified the diastereoisomers of 1,1,1,4,4,4-hexafluoro-*cis*-2,3-bis(methylphenylarsino)but-2-ene by examining the ^{1}H n.m.r. spectra of the respective binuclear iron complexes of the type $[(L\text{–}L)Fe_2(CO)_6]$.

We hereby report the results of our study on the preparation, identification, and resolution into enantiomers of the new ligand *o*-phenylenebis(methylphenylarsine), (I).

RESULTS AND DISCUSSION

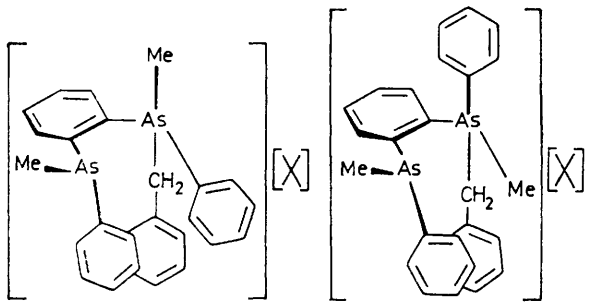
Preparation of o-*Phenylenebis(methylphenylarsine)*, (I).—The methylphenylarsenide ion, which is readily formed by the interaction of sodium metal with iodomethylphenylarsine in tetrahydrofuran (thf) as solvent, reacts exothermally with *o*-dichlorobenzene in a convenient reaction to give *o*-phenylenebis(methylphenylarsine) (I) as a high boiling yellow oil, b.p. 180—185 °C (0.05 mmHg) (65—72%),* which partially solidifies with time. Careful distillation of the reaction mixture from a particular run revealed the presence of eight side-products from this reaction, namely dimethylphenylarsine (III), b.p. 30—32 °C (0.5 mmHg) (5%), ethoxymethylphenylarsine (IV), b.p. 38 °C (0.5 mmHg) (0.8%), methyldiphenylarsine (V), b.p. 95—100 °C (0.5 mmHg) (5.6%), 1-chloro-2-(methylphenylarsino)benzene (VI), b.p. 135—140 °C (0.5 mmHg) (1.3%), methylphenylarsinic acid (VII), b.p. 151—152° C (0.1 mmHg) (4.1%), and 1,2-dimethyl-1,2-diphenyldiarsane (VIII), b.p. 158—160 °C (0.1 mmHg) (1%). The final fraction consisted of an equimolar mixture of *meso*-(Ia) and *racemic*-(Ib), b.p. 180—185 °C (0.05 mmHg) (70.5%). The side products (III), (IV), (V), (VII), and (VIII) were characterised by a comparison of their ^{1}H n.m.r. and mass spectra with authentic samples prepared by published procedures. Compound (VI) was identified on the basis of spectroscopic data and a microanalysis. A small amount of the unusual compound 1,3-dimethyl-1,2,3-triphenyltriarsane, (IX), also appeared to form in the reaction and co-distilled with the diastereoisomers (Ia) and (Ib) from which it was readily separated by fractional crystallisation from carbon tetrachloride. The mass spectrum of the residue from the distillation exhibited an intense signal at *m/e* 456. This was assigned the structure, 5,10-dihydro-5,10-diphenylarsanthren, (X). No attempt was made to isolate this material. The overall reaction is summarised in Scheme 1 and may be compared with the products obtained by Feltham [compounds (XI)—(XIV) in ref. 8] in analogous reactions of the dimethylarsenide ion.

Separation of the Diastereoisomers.—The presence of the two diastereoisomers (Ia) and (Ib) is clearly evident in the ^{1}H n.m.r. spectrum of the high-boiling fraction. Dilution of the oil in n-hexane followed by cooling of the solution in solid CO_2–acetone caused precipitation of white needles of the crude *racemic*-isomer, (Ib), which was obtained pure after one crystallisation from boiling ethanol, m.p. 88—88.5 °C. The mother liquors from the n-hexane and ethanol solutions, from which (Ib) had



SCHEME 1 (*i*), thf

been isolated, when combined and the solvents removed *in vacuo*, left an oil which was shown by its ^{1}H n.m.r. spectrum to consist of *ca.* 90% of the *meso*-isomer, (Ia), and 10% of (Ib). It was not possible to obtain pure (Ia) by fractional crystallisation alone; it was necessary to first form the benzylarsonium salts from the impure oil and to fractionally crystallise these. Accordingly, the residual oil was treated with an excess of benzyl bromide in benzene solution and produced, after 6 h standing at room temperature, white crystals of the pure arsonium bromide (XVa); this, after metathesis with sodium perchlorate, gave the corresponding air-stable perchlorate (XVIa) which after recrystallisation from acetone yielded the pure *erythro*-salt (XVIa). The reaction of either (Ia) or (Ib) with an excess of benzyl



erythro–(*RR*, *SS*) (XVa) X = Br (XVIa) X = ClO_4

threo–(*RS*, *SR*) (XVb) X = Br (XVIb) X = ClO_4

bromide under vigorous conditions did not give the corresponding dibenzyldiarsonium bromides. Mann [9] had earlier shown that although bromomethane readily quaternises one of the two arsenic atoms in *o*-phenylenebis(dimethylarsine), (II), stronger conditions were required to quaternise the remaining arsenic atom. In the case of the diarsines (Ia) and (Ib) it appears that the deactivating effect of one $[-As(Me)(CH_2Ph)(Ph)]^+$ group is too great to allow formation of *diarsonium* species.

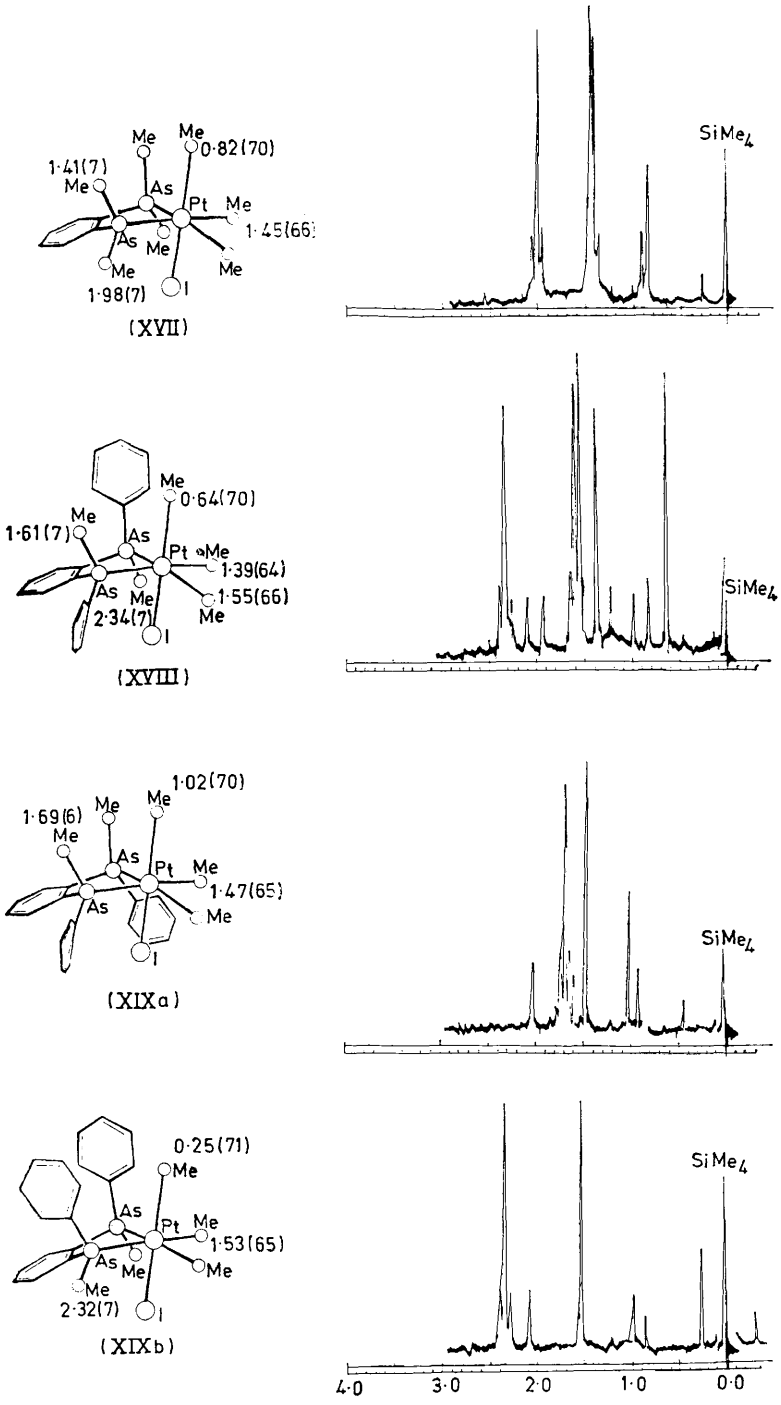
* 1 mmHg ≈ 13.6 × 9.8 Pa, 1M = 1 mol dm^{-3}.

[8] R. D. Feltham, A. Kassenally, and R. S. Nyholm, *J. Organometallic Chem.*, 1967, **7**, 285; R. D. Feltham and W. Silverthorn, *Inorg. Synth.*, 1967, **10**, 159; R. D. Feltham and H. G. Metzger, *J. Organometallic Chem.*, 1971, **33**, 347.

[9] F. G. Mann and F. C. Baker, *J. Chem. Soc.*, 1952, 4142.

Reduction of the arsonium perchlorates (XVIa) or (XVIb) with lithium tetrahydridoaluminate simply cleaves the benzyl linkage, toluene and the free diarsines (Ia) and (Ib) being liberated in a reaction entirely analogous to that developed by Horner [10] in the resolution of tertiary arsines.

Identification of the Diastereoisomers by Complex Formation.—Careful work by Shaw [11] has established the stereochemistry of complexes of the type $[PtX(R)(Me_2)L_2]$ (X = halide ion, R = alkyl group, and L = a tertiary arsine or phosphine) by means of ^1H n.m.r. spectroscopy. The chemical shifts and coupling constants, J(Pt–H), observed in this work are indicative of the con-



Structure of the *fac*-(diarsine)iodotrimethylplatinum(IV) complexes and 60 MHz ^1H n.m.r. assignment of methyl resonances (δ/p.p.m., J/Hz in parentheses)

[10] L. Horner and M. Ernst, *Chem. Ber.*, 1970, **103**, 318.
[11] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2801, 2964.

figuration adopted by a particular complex. For example J(Pt–H) lies within the ranges 69—73 (*trans*-X), 60—66.5 (*trans*-arsenic), and *ca.* 44 Hz (*trans*-methyl) for the above mentioned complexes when L is a tertiary arsine. More recently, Cheney and Shaw [6] extended these criteria to include analogous complexes formed by the chelating diarsine 1,2-bis(methylphenylarsino)ethane.

A simple method of preparing complexes of the type $[PtMe_3(I)(diarsine)]$ has been employed in this work in place of the one developed by Shaw and his co-workers which involved oxidative addition of iodomethane across the square-planar complexes $[PtMe_2(diarsine)]$.[6] Treatment of $[PtMe_3I]$ with (II) in benzene solution [12] gave crystalline yellow *fac*-iodotrimethyl[*o*-phenylenebis(dimethylarsine)]platinum(IV), (XVII), which was characterised by a comparison of its ^1H n.m.r. spectrum with a sample obtained by the alternative oxidative addition.[6] Similarly, addition of (Ib) to $[PtMe_3I]$ gave a good yield of the pale yellow crystalline adduct (XVIII). Five singlets of equal intensity with platinum satellites were observed in the ^1H n.m.r. spectrum of this complex and an analysis of the spectrum reveals that the complex contains the *racemic*-diarsine and has the *fac*-configuration.

The interaction of (Ia) under the same reaction conditions gave a yellow product of composition $[PtMe_3(I)\{o\text{-}C_6H_4(AsMePh)_2\}]$ which was subsequently shown to consist of an equimolar mixture of the two isomers (XIXa) and (XIXb). Recrystallisation of the isomeric mixture from dichloromethane–n-hexane solution separated the two complexes and each isomer when purified showed in its ^1H n.m.r. spectrum three singlets of intensity 2 : 2 : 1 with platinum satellites. These data are consistent with the *fac*-configuration containing the *meso*-diarsine in both cases. The position of the chemical shifts of the *trans*-Pt–Me groups, however, also enabled configuration (XIXa) to be assigned to the less soluble isomer in dichloromethane–n-hexane and (XIXb) to the more soluble complex, chemical shifts for the *trans*-Pt–Me resonances occurring at δ 1.02 and 0.25 p.p.m. respectively. In structure (XIXb) the *trans*-methyl group is situated adjacent to two As–Ph rings (Figure), and is thus shielded in relation to the same groups in (XIXa) where this methyl group is adjacent to the As–Me groups. Isomer (XIXb) was also obtained in a stereospecific oxidative addition between iodomethane and *cis*-dimethyl[*meso*-*o*-phenylenebis(methylphenylarsine)]-platinum(II), (XXIa), the latter being prepared from the corresponding *cis*-dichloroplatinum(II) complex (XXa) and methyl-lithium. This observation agrees with the findings of Cheney and Shaw [6] using 1,2-bis(methylphenylarsino)ethane.

A stereospecific reaction also occurs when either of the neutral octahedral complexes (XVII), (XVIII), (XIXa), or (XIXb) is treated with pyridine (py) in the presence [12] of $Ag[PF_6]$ in acetone solution. Silver(I) iodide rapidly precipitated and the cations (XXII), (XXIII), (XXIVa), and (XXIVb) were isolated as white crystals from the filtrate after AgI had been removed. The ^1H n.m.r. spectra of solutions of these salts showed that the *fac*-

$$[PtMe_3(I)(diarsine)] \xrightarrow[AgPF_6]{py,acetone} [PtMe_3(diarsine)(py)][PF_6] + AgI \quad (1)$$

configuration found in the neutral complexes is maintained in the cations and that there appears to be no overall change in the stereochemistry of the products, complexes (XIXa) and (XIXb) giving as the sole products (XXIVa) and (XXIVb) respectively.

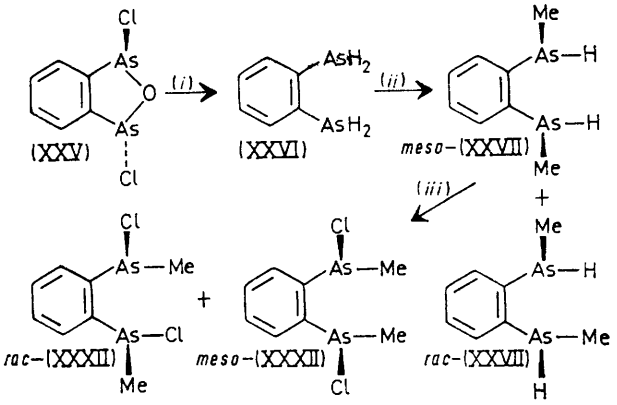
Steric Course of Reactions in the Formation of o-*Phenylenediarsines.*—Reduction of *o*-phenylenediarsonic acid with sulphur dioxide in concentrated hydrochloric acid using potassium iodide as catalyst gives, as the only product, *trans*-1,3-dichloro-1,3-dihydro-2,1,3-benzoxadiarsole, (XXV).[13] A crystal-structure determination of this molecule has shown that it has the *trans*(*racemic*) configuration.[14] It therefore seemed of interest to examine some further reactions of the *o*-phenylenediarsine nucleus.

Oxidation of (II) with bromine (1 : 8) in carbon tetrachloride solution yielded *o*-phenylenebis(dibromodimethylarsine), (XXVIII), as a yellow granular solid. The solid-state thermal elimination of bromomethane from this As^V species followed by distillation of the residue produced *o*-phenylenebis(bromomethylarsine), (XXIX), in good yield (73%) as a white semi-solid material. The ^1H n.m.r. spectrum of (XXIX) showed one sharp singlet at δ 2.08 p.p.m. for the As–Me resonance which could not be resolved further, even with a sweep width of 2 Hz cm^{-1} at 90 MHz. The corresponding diiodide, (XXXI), was isolated as yellow cubes, m.p. 84—84.5 °C, from a metathetical reaction of the dibromide with KI in acetone. Again, the 90 MHz ^1H n.m.r. spectrum of (XXXI) showed only one sharp singlet at δ 2.20 p.p.m. for the As–Me resonance. The high quadrupole moment of the ^{75}As nucleus causes rapid relaxation of the spin system and results in relatively narrow linewidths for protons of groups attached to arsenic nuclei. Consequently, with such small linewidths, even small chemical shifts were readily observed in the ^1H n.m.r. spectra of these compounds. These observations support the view that elimination of bromomethane from (XXVIII) is a stereospecific reaction leading to only one of the two possible diastereoisomers of (XXIX). In addition, the resulting diastereoisomer is recovered unchanged from reactions which normally racemise tertiary arsines. Thus, a sample of the dibromide when heated under reflux for 18 h in an ethanol solution containing aqueous hydrobromic acid (49%) was recovered unchanged.

The original mechanism proposed by Horner [15] for racemisation of tertiary arsines by mineral acids involves formation of an arsonium salt. Doak and Freedman [16]

[12] H. C. Clark and L. E. Mazer, *Inorg. Chem.*, 1973, **12**, 362.
[13] L. Kalb, *Annalen*, 1921, **432**, 74.
[14] W. R. Cullen and J. Trotter, *Canad. J. Chem.*, 1962, **40**, 1113.
[15] L. Horner and W. Hofer, *Tetrahedron Letters*, 1966, 3323.
[16] G. O. Doak and L. D. Freedman, 'The Organometallic Chemistry of Arsenic, Antimony and Bismuth,' Wiley–Interscience, New York, 1970, pp. 159—160.

suggested the formation of a neutral trigonal-bipyramidal intermediate which undergoes rapid pseudo-rotation.[17] We examined molecular models of the oxidised species (XXVIII) and showed, after placing the bromine atoms in their preferred axial positions [18] on the As^V nuclei, that the sterically favoured configuration of this molecule is unlikely to undergo pseudo-rotation. Provided steric considerations govern this reaction, it is evident that elimination of the two most hindered bromomethane molecules will produce the *trans*- or *racemic*-dibromo-species. The failure to racemise the dibromo-compound (XXIX) may also be interpreted in terms of stereospecific addition and subsequent elimination of HBr from a preferred five-co-ordinate intermediate *via* the least-hindered path. Recent work in the stereochemistry of eliminations from organic compounds in the solid state has shown a high degree of selectivity in the geometry of



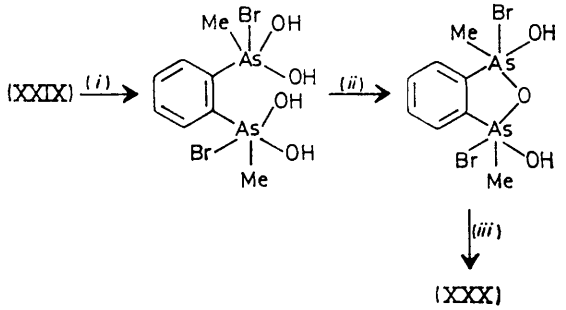
SCHEME 2 (*i*), $Li[AlH_4]$; (*ii*), $LiBu^n$ and MeI; (*iii*), CCl_4

the products.[19] For example, photoelimination of carbon monoxide from *cis*- or *trans*-1,3-diphenylindan-2-one to give *cis*- or *trans*-1,2-diphenylbenzocyclobutane respectively proceeds in 95% yield in the solid state, but when this reaction is carried out in solution both isomeric indanones yield *trans*-1,2-diphenylbenzocyclobutane (*ca.* 90%).[20] The possibility of the As–Me singlet in the ^1H n.m.r. spectrum of (XXIX) resulting from rapid inversion of the pyrimidal arsenic atoms allowing interconversion between the *meso*- and *racemic*-isomers is discounted on the basis that treatment of *o*-phenylenebis(methylarsine), (XXVII) [derived [21] from reaction of *o*-phenylenediarsine, (XXVI), with n-butyl-lithium followed by iodomethane], with carbon tetrachloride produces both diastereoisomers of *o*-phenylenebis(chloromethylarsine), (XXXII). The ^1H n.m.r. spectra of (XXVII) and (XXXII) obtained by this method showed two As–Me resonances in each case corresponding to the *meso*- and *racemic*-isomers (Scheme 2).

The reduction of compound (XXIX) with $Li[AlH_4]$ produced only one of the two possible diastereoisomers of the secondary arsine (XXVII). Again, the reaction of (XXVII), obtained by hydride reduction of (XXIX), with carbon tetrachloride is a stereospecific process giving only one of the two possible diastereoisomers of (XXXII). Attempts to isomerise compound (XXIX) by forming the oxygen-bridged compound, 1,3-dihydro-1,3-dimethyl-2,1,3-benzoxadiarsole, (XXXIII) (either by treatment with sodium cyanide [22] or with sodium hydroxide) again produced only one of the two possible diastereoisomers of this heterocycle. The reaction of compound (XXXIII) with thionyl chloride also resulted in formation of only one diastereoisomer of (XXXII). The remarkable stability of the *racemic* stereochemistry to racemisation is also demonstrated by reaction of compound (XXIX) with 2 mol of diethylamine followed by cleavage of the aminoarsine intermediate with dry hydrogen chloride; again the reactions were stereospecific and only *racemic*-(XXXII) was isolated.

Treatment of compound (XXIX) with phenyl-lithium or phenylmagnesium bromide was non-stereospecific, however, and gave in each case an equal mixture of (Ia) and (Ib). An equimolar mixture of the diastereoisomers (Ia) and (Ib) was also formed when (XXXI) was reduced with sodium metal in thf and the resulting dianion treated with bromobenzene.

Recrystallisation of compound (XXIX) from carbon tetrachloride produced a white crystalline material of elemental composition $C_6H_4As_2Br_2O$. This material was shown to be *trans*-1,3-dibromo-1,3-dihydro-2,1,3-benzoxadiarsole, (XXX), by crystallographic studies.[23] The ready formation of the (XXX) provides a striking example of the general stability of these five-membered arsenic-ring systems.[24] The mechanism of cyclisation is inferred from the observation that methanol is the by-product of this reaction [from the ^1H n.m.r. spectrum of a sample of (XXIX) dissolved in carbon tetrachloride containing a trace of water]. A possible mechanism for this



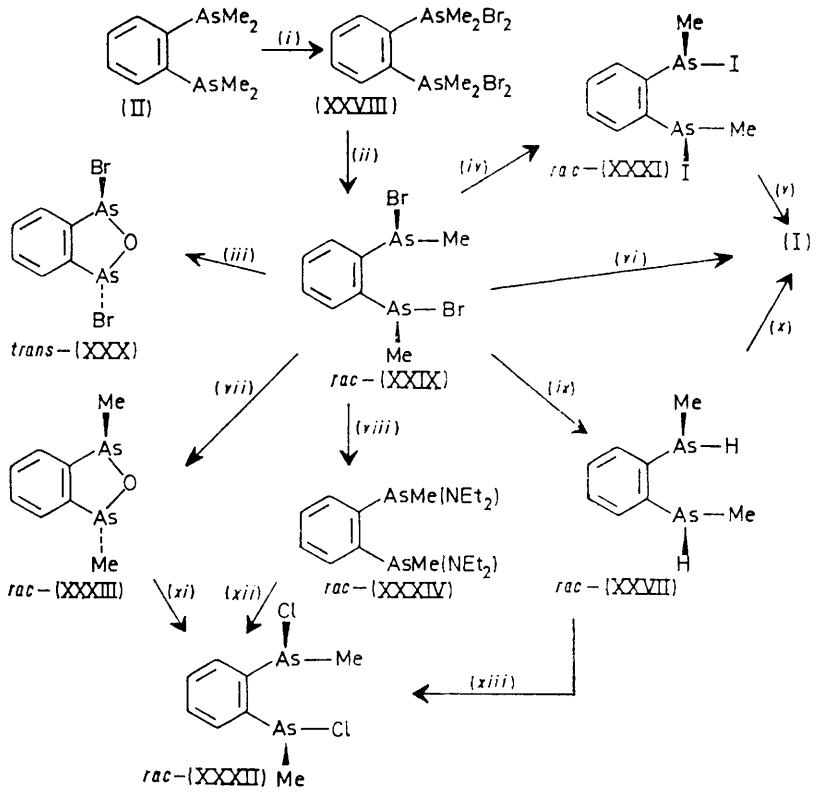
SCHEME 3 (*i*), O_2 and H_2O; (*ii*), $-H_2O$; (*iii*), —MeOH

reaction involves oxidation of (XXIX) to the bis[dihydroxoarsenic(v)] [25] species which then undergoes dehydration and elimination of methanol (Scheme 3).

[17] F. H. Weistheimer, *Accounts Chem. Res.*, 1968, **1**, 70.
[18] D. J. Sutor and F. R. Harper, *Acta Cryst.*, 1959, **12**, 585.
[19] M. D. Cohen and B. S. Green, *Chem. in Britain*, 1973, **9**, 490.
[20] G. Quinkert, T. Tabata, E. A. J. Hickman, and W. Dobrat, *Angew. Chem. Internat. Edn.*, 1971, **10**, 199.
[21] T. C. Carlton and C. D. Cook, *Inorg. Chem.*, 1971, **10**, 2628.
[22] H. Brintzinger and A. Scholz, *Chem. Ber.*, 1950, **83**, 141.
[23] J. C. Dewan, K. Henrick, A. H. White, and S. B. Wild, *Austral. J. Chem.*, 1975, **28**, 15.
[24] F. G. Mann, 'The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, and Bismuth,' Wiley–Interscience, New York, 1970, pp. 532—539.
[25] D. S. Tarbell and J. R. Baughan, *J. Amer. Chem. Soc.*, 1945, **67**, 41.

The chemical transformations discussed above are summarised in Scheme 4.

Resolution of racemic-o-*Phenylenebis(methylarsine)*, (Ib).—The resolution of (Ib) was effected by separating the diastereoisomeric salts formed in the reaction of the salt (XVb) with sodium D(−)-dibenzoylhydrogentartrate in aqueous methanol. The mixture of diastereoisomeric salts was obtained initially as an oil but fractionally crystallised from isopropyl alcohol–diethyl ether solutions under anhydrous conditions. The crystalline tartrate salts are hygroscopic and rapidly form an oil when exposed to the atmosphere. The separated tartrate salts, (±)- and (=)-(XXXV), on metathesis with $K[PF_6]$ produced the corresponding air-stable hexafluorophosphate salts (+)- and (−)-(XXXVI), α(293.15 K, 589.3 nm) +3.1 and −2.8°, respectively, which after reduction with $Li[AlH_4]$ in thf solutions yielded the corresponding enantiomers of (Ib), α(293.15 K, 589.3 nm) + 31.4 and −24.3°, respectively.



SCHEME 4 (*i*), Br_2 and CCl_4; (*ii*), Heat, −MeBr; (*iii*), aerial oxidation; (*iv*), KI, acetone; (*v*), Na, PhBr; (*vi*), PhMgBr or PhLi; (*vii*), NaOH or NaCN; (*viii*), Et_2NH; (*ix*), $Li[AlH_4]$; (*x*), Bu^nLi, PhBr; (*xi*), $SOCl_2$; (*xii*), HCl (g); (*xiii*), CCl_4

EXPERIMENTAL

All reactions were carried out in an atmosphere of pure nitrogen using the Schlenk technique. Solvents were dried in the usual way and degassed by distillation through a stream of pure nitrogen.

Microanalyses were carried out by the Australian Microanalytical Service, Melbourne. ^1H N.m.r. spectra were recorded at 60 MHz using a Varian A-60 spectrometer and where indicated at 90 MHz using a Bruker HX-90 spectrometer; chemical shifts were measured relative to tetramethylsilane as internal standard. The polarimetric readings were made using a Perkin-Elmer 141 polarimeter and a 10 cm thermostatted cell at 20 °C. Mass spectra were recorded on a Varian-Mat CH4 spectrometer, the compounds being introduced directly into the ion source. The mass spectra of *meso-* and *racemic-o*-phenylenebis(methylphenylarsine), (Ia) and (Ib), *trans*-1,3-dichloro-1,3-dihydro-2,1,3-benzoxadiarsole, (XXV), *o*-phenylenediarsine, (XXVI), *o*-phenylenebis(methylarsine), (XXVII), and *o*-phenylenebis(bromomethylarsine), (XXIX), have been reported elsewhere.[26]

Iodomethylphenylarsine.—Methylphenylarsinic acid was prepared from phenylarsonic acid using the method of Hamilton and his co-workers [27] and then reduced with sulphur dioxide in concentrated hydrochloric acid containing a trace of potassium iodide. Metathesis of the *chloroarsine* with potassium iodide in acetone solution gave the iodoarsine, b.p. 108—110 °C (0.1 mmHg) (98%). ^1H N.m.r. spectrum (CCl_4): δ 2.13 (3 H, s, As–CH_3), 7.28 (3 H, br t, aromatics), and 7.65 p.p.m. (2 H, br q, aromatics).

Reaction of Methylphenylarsenide Anion with o-*Dichlorobenzene*.—A solution of iodomethylphenylarsine (100 g, 0.34 mol) in tetrahydrofuran (thf) (250 cm^3) was added dropwise to a well stirred suspension of finely divided sodium (23 g, 1.0 mol) in the same solvent (500 cm^3). The reaction commenced immediately and precipitation of sodium iodide and

[26] K. Henrick, D. L. Kepert, E. Shewchuk, K. R. Trigwell, and S. B. Wild, *Austral. J. Chem.*, 1974, **27**, 727.

[27] E. J. Cragoe, R. J. Andres, R. F. Coles, B. Elpern, J. F. Morgan, and C. S. Hamilton, *J. Amer. Chem. Soc.*, 1947, **69**, 925.

formation of a red solution were observed. The red colour in the solution, due to the presence of the methylphenylarsenide anion, serves as a monitor of the reaction. The red colour disappeared as more of the iodoarsine was added due to formation of the yellow intermediate 1,2-dimethyl-1,2-diphenyldiarsane which in turn is reduced to the red anion. In this way the reaction can be maintained under gently refluxing conditions by carefully titrating in the iodoarsine. When addition of the iodoarsine was complete the solution was cooled to room temperature and *o*-dichlorobenzene (25 g, 0.17 mol), dissolved in thf (200 cm^3), added at a rate which maintained the reflux. When addition was complete the reaction mixture was heated under reflux for 2 h, cooled in an ice-bath, and the reaction mixture hydrolysed with a saturated aqueous solution of ammonium chloride (100 cm^3). Diethyl ether (500 cm^3) was added to aid in separation of the organic layer which was separated and dried ($MgSO_4$). A deep red oil remained after the removal of the solvent and was fractionally distilled to give the following fractions which were identified as indicated.

Fraction (*i*). A colourless liquid, b.p. 30—32 °C (0.5 mmHg) (3.1 g, 0.017 mol, 5%), *dimethylphenylarsine*, (III). ^1H N.m.r. spectrum (CCl_4): δ 1.10 (6 H, s, As–CH_3), and 7.39 p.p.m. (5 H, m, aromatics). Mass spectrum: *m/e* 182 (94%, Me_2AsPh). Treatment of the liquid with iodomethane gave white crystals of the corresponding *methiodide*, m.p. 223—224 °C (lit.,[28] 224—225 °C). An authentic sample of (III) prepared from methylmagnesium iodide and dichlorophenylarsine gave identical ^1H n.m.r. and mass spectra to the above.

Fraction (*ii*). A pale yellow liquid, b.p. 38 °C (0.5 mmHg) (0.6 g, 0.0028 mol, 0.8%), *ethoxymethylphenylarsine*, (IV). ^1H N.m.r. spectrum (CCl_4): δ 1.12 (3 H, t, *J* 7, CH_2CH_3), 1.31 (3 H, s, As-CH_3), 3.66 (2 H, q, *J* 7 Hz, CH_2CH_3), and 7.38 p.p.m. (5 H, m, aromatics). Mass spectrum: *m/e* 212 [100%, Me(Ph)AsOEt)]. The ^1H n.m.r. and mass spectra were identical to those obtained from an authentic sample of (III) prepared from chloromethylphenylarsine and sodium ethoxide.

Fraction (*iii*). A colourless liquid, b.p. 95—100 °C (0.5 mmHg) (4.6 g, 0.019 mol, 5.6%), *methyldiphenylarsine*, (V). ^1H N.m.r. spectrum (CCl_4): δ 1.40 (3H, s, As–CH_3) and 7.26 p.p.m. (10 H, m, aromatics). Mass spectrum: *m/e* 244 (90%, $MeAsPh_2$). Treatment of this component with iodomethane gave white crystals of *dimethyldiphenylarsonium iodide*, m.p. 208—210 °C (lit.,[29] 211—213 °C). ^1H N.m.r. spectrum ($CDCl_3$): δ 2.84 (6 H, s, As^+–CH_3) and 7.80 p.p.m. (10 H, m, aromatics). An authentic sample of (V) was prepared from phenylmagnesium bromide and chloromethylphenylarsine and gave identical ^1H n.m.r. and mass spectra to the above.

Fraction (*iv*). A pale yellow liquid, b.p. 135—140 °C (0.5 mmHg) (1.2 g, 0.0043 mol, 1.3%), *1-chloro-2-methylphenylarsinobenzene*, (VI) (Found: C, 55.8; H, 4.1. $C_{13}H_{12}AsCl$ requires C, 56.0; H, 4.3%). ^1H N.m.r. spectrum (CCl_4): δ 1.43 (3 H, s, As–CH_3) and 7.28 p.p.m. (9 H, unsym. m, aromatics). Mass spectrum: *m/e* 278 and 280 (34%, $MePhAs{\cdot}C_6H_4Cl$).

Fraction (*v*). A colourless liquid which solidified on standing, b.p. 151—152 °C (0.1 mmHg) (2.8 g, 0.014 mol, 4.1%), *methylphenylarsinic acid*, (VII). Crystallisation from chloroform gave white needles, m.p. 175—176 °C (lit.,[24] 179—179.5 °C) (Found: C, 41.8; H, 4.7. $C_7H_9AsO_2$ requires C, 41.9; H, 4.5%). ^1H N.m.r. spectrum ($CDCl_3$): δ 1.98 (3 H, s, As–CH_3), 7.71 (5H, m, aromatics), and 10.01 p.p.m. (1 H, s, OH). The ^1H n.m.r. spectrum and m.p. of fraction (v) were identical to those of an authentic sample of (VII).[24]

Fraction (*vi*). A pale yellow liquid which solidified on standing, b.p. 158—160 °C (0.1 mmHg) (1.2 g, 0.0036 mol, 1%), 1,2-dimethyl-1,2-diphenyldiarsane, (VIII). Recrystallisation from carbon tetrachloride gave white crystals, m.p. 80.5—83 °C (lit.,[30] 81.5—82 °C). ^1H N.m.r. spectrum ($CDCl_3$): δ 0.70 (3 H, s, As–CH_3), 0.78 (3 H, s, As–CH_3), 0.78 (3 H, s, As–CH_3), and 6.85 p.p.m. (10 H, m, aromatics). Mass spectrum: *m/e* 334 [22%, $(MePhAs)_2$]. An authentic sample of (VIII), prepared by the method of Reesor and Wright,[30] gave identical ^1H n.m.r. and mass spectra to the above.

Fraction (*vii*). A yellow syrup, b.p. 180—185 °C (0.05 mmHg) (48.6 g, 0.12 mol, 70.5%), meso- and racemic-*o-phenylenebis(methylphenylarsine)*, (Ia) and (Ib). ^1H N.m.r. spectrum (CCl_4): δ 1.23 (6H, s, As–CH_3), 1.41 (6H, s, As–CH_3), and 7.46 p.p.m. (28H, m, aromatics). The ^1H n.m.r. spectrum of this fraction showed it to consist of an equal mixture of the two isomers (Ia) and (Ib). It also indicated the presence of a minor impurity which was separated by dissolving the oil in carbon tetrachloride and filtering off the small quantity of insoluble material. This solid, fraction (viia) (120 mg, 2.5 mmol), crystallised from chloroform as glistening white plates, m.p. 124—125.5 °C (Found: C, 49.6; H, 4.0. $C_{20}H_{21}As_3$ requires C, 49.4; H, 4.3%). ^1H N.m.r. spectrum ($CDCl_3$): δ 0.69 (3 H, s, As–CH_3), 0.72 (3 H, s, As–CH_3), and 7.05 p.p.m. (15 H, m, aromatics). Mass spectrum: *m/e* 486 (12%, $C_{20}H_{21}As_3$). This compound was assigned as 1,3-*dimethyl*-1,2,3-*triphenyltriarsane*, (IX). The residue from the distillation was found by ^1H n.m.r. spectroscopy not to contain arsenic–methyl groups and the mass spectrum indicated the presence of 5,10-*dihydro*-5,10-*diphenylarsanthren*, (X), *m/e* 456.

racemic-o-*Phenylenebis(methylphenylarsine)*, (Ib).—The partly solidified oil from fraction (vii) (see above) was dissolved in n-hexane (150 cm^3) and the solution cooled in a solid CO_2–acetone bath. A white solid deposited from the solution and was collected by decanting the n-hexane mother liquor and then redissolved in hot ethanol (220 cm^3) whereupon white needles of (Ib) formed on cooling. These were collected by filtration and dried *in vacuo*, m.p. 88—88.5 °C (22g, 0.054 mol, 90.4%) (Found: C, 58.6; H, 4.9. $C_{20}H_{20}As_2$ requires C, 58.5; H, 4.8%). ^1H N.m.r. spectrum ($CDCl_3$): δ 1.25 (6 H, s, As-CH_3) and 7.40 (14 H, m, aromatics). Pure (Ib) is insoluble in carbon tetrachloride.

The mother liquors from the n-hexane and ethanol solutions, from which (Ib) was obtained, were combined and the solvents removed to leave an oil (26 g). The ^1H n.m.r. spectrum of the latter showed it to be a mixture of *ca.* 90% of the *meso*-isomer (Ia) and the remaining quantity of (Ib) which could not be separated by repeated fractional crystallisation.

threo-*Benzyl(methyl)[(2-methylphenylarsino)phenyl]phenylarsonium Bromide*, (XVb), *and Perchlorate Monohydrate*, (XVIb).—Benzyl bromide (1.8 g, 0.01015 mol) was added to a benzene solution (25 cm^3) of (Ib) (4.1 g, 0.01 mol). The mixture was allowed to stand at room temperature for 6 h whereupon white crystals deposited. These were collected, washed with diethyl ether, and recrystallised

[28] E. R. H. Jones and F. G. Mann, *J. Chem. Soc.*, 1955, 4472.
[29] G. E. Razuveav, V. S. Malinouskii, and D. A. Godina, *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 721.
[30] J. W. B. Reesor and G. F. Wright, *J. Org. Chem.*, 1957, **22**, 382.

from acetone–ether to give white needles of *compound* (XVb), m.p. 164—165 °C (5.4 g, 0.0093 mol, 93%) (Found: C, 55.5; H, 4.4. $C_{27}H_{27}As_2Br$ requires C, 55.7; H, 4.6%). ^1H N.m.r. spectrum ($CDCl_3$): δ 1.31 (3 H, s, As–CH_3), 2.75 (3 H, s, As^+–CH_3), 5.11, 5.29 (2 H, ABq, *J* 12.5 Hz, CH_2–As^+), and 7.5 p.p.m. (19 H, complex m, aromatics).

The reaction of (Ib) with an excess of benzyl bromide in refluxing benzene solution for 24 h or neat at 140 °C for 18 h in a sealed tube gave only the arsonium bromide (XVb) with no detectable amounts of the diarsonium bromide. Salt (XVb) was found to be very hygroscopic and for ease of handling was converted to the corresponding perchlorate by metathesis with sodium perchlorate in acetone. Recrystallisation of the crude product from acetone gave *compound* (XVIb) as white crystals, m.p. 198—200 °C (Found: C, 52.5; H, 4.5. $C_{27}H_{29}As_2ClO_5$ requires C, 52.4; H, 4.7%). ^1H N.m.r. spectrum (CD_3COCD_3): δ 1.33 (3H, s, As–CH_3), 2.64 (3 H, s, As^+–CH_3), 4.85 (2 H, br s, CH_2–As^+), 7.40 (10 H, m, aromatics), and 7.72 p.p.m. (9 H, m, aromatics).

Lithium Tetrahydridoaluminate Reduction of (XVIb).—A suspension of $Li[AlH_4]$ (0.4 g, 0.01 mol) in thf (50 cm^3) was added dropwise to a stirred suspension of (XVIb) (6.1 g, 0.01 mol) in thf (100 cm^3) and the mixture heated under reflux for 12 h. The solution was then cooled in an ice-bath and hydrolysed with a solution of sodium hydroxide (0.1M, 100 cm^3), diethyl ether added (50 cm^3), and the organic layer separated and dried ($MgSO_4$). Removal of the organic solvents under reduced pressure left a white solid which after recrystallisation from hot ethanol (40 cm^3) gave pure (Ib), m.p. 87—88 °C (3.2 g, 0.008 mol, 78%) (Found: C, 58.1; H, 4.8; As, 36.7. $C_{20}H_{20}As_2$ requires C, 58.5; H, 4.8; As, 36.6%). The ^1H n.m.r. spectrum was identical to that found for (Ib) prepared above.

erythro-*Benzyl(methyl)*[(2-*methylphenylarsino*)*phenyl*]-*phenylarsonium Perchlorate Monohydrate*, (XVIa).—The oil obtained from the residue (26 g) after isolating (Ib) (see above) was dissolved in benzene (150 cm^3) and benzyl bromide (17.1 g, 0.1 mol) added. The solution was left to stand at room temperature for 12 h during which time a pale yellow gummy material formed. The benzene was removed by distillation under reduced pressure and the residue washed with diethyl ether and then dissolved in acetone and added to a solution containing an excess of $NaClO_4$ in aqueous acetone. The mixture was shaken for 0.5 h, most of the acetone removed under reduced pressure, and the perchlorate salt extracted into dichloromethane and the solution dried ($MgSO_4$). Removal of the dichloromethane *in vacuo* yielded a solid which was dissolved in the minimum quantity of ethanol and reprecipitated by dropwise addition of diethyl ether to yield white crystals of the *perchlorate* (XVIa), m.p. 178—181 °C (25.4 g, 0.041 mol, 68%) (Found: C, 52.3; H, 4.6. $C_{27}H_{29}As_2ClO_5$ requires C, 52.4; H, 4.7%). ^1H N.m.r. spectrum ($CDCl_3$): δ 1.20 (3 H, s, As–CH_3), 2.50 (3 H, s, As^+–CH_3), 4.81 (2 H, br s, CH_2–As^+), 7.40 (10 H, m, aromatics), and 7.72 (9 H, m, aromatics).

meso-o-*Phenylenebis(methylphenylarsine)*, (Ia).—A suspension of $Li[AlH_4]$ (1.6 g, 0.04 mol) in thf (200 cm^3) was added dropwise to a stirred suspension of (XVIa) (24 g, 0.04 mol) in thf (500 cm^3). The mixture was heated under reflux for 20 h and worked-up as described above to leave an oil (16 g) which after distillation afforded meso-o-*phenylenebis(methylphenylarsine)*, (Ia) (13.6 g, 0.033 mol, 83%), as a colourless syrup, b.p. 184—186° (0.05 mmHg) (Found: C, 58.8; H, 4.9. $C_{20}H_{20}As_2$ requires C, 58.5; H, 4.8%). ^1H N.m.r. spectrum (CCl_4): δ 1.41 (6 H, s, As–CH_3) and 7.46 p.p.m. (14 H, m, aromatics).

erythro-*Benzyl(methyl)*[(2-*methylphenylarsino*)*phenyl*]-*phenylarsonium Bromide*, (XVa).—Compound (Ia) (4.1 g, 0.01 mol) was dissolved in benzene (50 cm^3) and benzyl bromide (1.8 g, 0.0105 mol) added. The reaction mixture was left to stand for 3 h and the resulting crystals collected by filtration, washed with diethyl ether, and recrystallised from acetone–ether to give the *bromide* (XVa) as small white cubes, m.p. 132—133 °C (5.3 g, 0.009 mol, 93%) (Found: C, 55.5; H, 4.6. $C_{27}H_{27}As_2Br$ requires C, 55.7; H, 4.6%). ^1H N.m.r. spectrum ($CDCl_3$): δ 1.18 (3 H, s, As–CH_3), 2.54 (3 H, s, As^+–CH_3), 5.04 (2 H, br s, CH_2–As^+), and 7.50 p.p.m. (19 H, m, aromatics). Treatment of (Ia) with an excess of benzyl bromide either in boiling benzene for 24 h or neat in a sealed tube for 18 h at 140 °C gave only (XVa) with no detectable amounts of the diarsonium bromide.

cis-*Dichloro*[racemic-o-*phenylenebis(methylphenylarsine)*]-*platinum*(II), (XXb).—With potassium tetrachloroplatinate(II) in water and (Ib) in ethanol white needles were obtained from dichloromethane–n-hexane, m.p. 297—300 °C (93%) (Found: C, 35.7; H, 3.0. $C_{20}H_{20}As_2Cl_2Pt$ requires C, 35.5; H, 2.9%). ^1H N.m.r. spectrum (CH_2Cl_2): δ 1.76 [s, *J*(Pt–H) 7.0 Hz, As–CH_3].

Prepared similarly were: cis-*dichloro*[meso-o-*phenylenebis(methylphenylarsine)*]*platinum*(II), (XXa), prisms from cyclohexane–dichloromethane, m.p. 276—280 °C (91%) (Found: C, 35.2; H, 3.1; As, 22.5. $C_{20}H_{20}As_2Cl_2Pt$ requires C, 35.5; H, 2.9; As, 22.2%), δ (in CH_2Cl_2) 1.93 p.p.m. [s, *J*(Pt–H) 6.5 Hz, As–CH_3]; cis-*dichloro*[racemic-o-*phenylenebis(methylphenylarsine)*]*palladium*(II), (XXXVIIb), yellow prisms from cyclohexane–dichloromethane, m.p. 310—315 °C (87%) (Found: C, 40.8; H, 3.5. $C_{20}H_{20}As_2Cl_2Pd$ requires C, 40.8; H, 3.4%), δ (in $CDCl_3$) 2.20 p.p.m. (s, As–CH_3); and cis-*dichloro*[meso-o-*phenylenebis(methylphenylarsine)*]*palladium*(II), (XXXVIIa), yellow plates from chloroform–cyclohexane, m.p. 290—296 °C (79%) (Found: C, 40.8; H, 3.3. $C_{20}H_{20}As_2Cl_2Pd$ requires C, 40.8; H, 3.4%), δ (in $CDCl_3$) 2.39 p.p.m. (s, As–CH_3).

fac-*Iodotrimethyl*[o-*phenylenebis(dimethylarsine)*]*platinum*-(IV), (XVII).—A benzene solution (10 cm^3) of iodotrimethylplatinum(IV) [31] (360 mg, 1 mmol) was treated with *o*-phenylenebis(dimethylarsine), (II) [8] (280 mg, 1 mmol). The solution was stirred for 10 min and then the volume of benzene was reduced to 2 cm^3. Careful addition of diethyl ether to the solution gave yellow crystals of *complex* (XXVI), m.p. 180—182 °C (630 mg, 0.9 mmol, 98.5%) (lit.,[6] 179—183 °C) (Found: C, 24.0; H, 3.9. $C_{13}H_{25}As_2IPt$ requires C, 23.9; H, 3.8%).

fac-*Iodotrimethyl*[racemic-o-*phenylenebis(methylphenylarsine)*]*platinum*(IV), (XVIII), was prepared as above, m.p. 300—304 °C (96%) (Found: C, 35.7; H, 4.0. $C_{23}H_{29}As_2IPt$ requires C, 35.5; H, 3.7%).

fac-*Iodotrimethyl*[meso-o-*phenylenebis(methylphenylarsine)*]*platinum*(IV), (XIXa) *and* (XIXb).—This complex was prepared as above as a pale yellow solid consisting of an approximately equal mixture of two isomers as indicated by ^1H n.m.r. spectroscopy. Fractional crystallisation of the mixture from dichloromethane–n-hexane gave (XIXa), m.p. 247—250 °C (18%) (Found: C, 35.8; H, 3.9. $C_{23}H_{29}As_2IPt$ requires C, 35.5; H, 3.7%), and evaporation of the filtrate followed by recrystallisation of the residue from ethanol gave (XIXb), m.p. 268—274 °C (29%) (Found: C, 35.8; H, 3.9. $C_{23}H_{29}As_2IPt$ requires C, 35.5; H, 3.7%).

[31] D. E. Clegg and J. R. Hall, *Inorg. Synth.*, 1967, **10**, 71.

cis-*Dimethyl*[meso-o-*phenylenebis(methylphenylarsine)*]-*platinum*(II), (XXI).—This complex was prepared from finely powdered (XXa) and methyl-lithium, according to ref. 6, as white plates (86%) after recrystallisation from ethanol, m.p. 204—206 °C (Found: C, 41.3; H, 3.8. $C_{22}H_{26}As_2Pt$ requires C, 41.5; H, 4.1%). ^{1}H N.m.r. spectrum ($CDCl_3$): δ 0.84 [6 H, s, *J*(Pt–H) 76, Pt–CH_3] and 1.39 p.p.m. [6 H, s, *J*(Pt–H) 11.0 Hz, As–CH_3].

Addition of Iodomethane to Complex (XXI).—From (XXI) and iodomethane in a sealed tube after 48 h, recrystallisation from ethanol gave (XIXb), m.p. 267—273 °C (91%) (Found: C, 35.9; H, 3.4. $C_{23}H_{29}As_2IPt$ requires C, 35.5; H, 3.7%). This material was the sole product.

fac-*Trimethyl*[o-*phenylenebis(dimethylarsine)*]*pyridine-platinum*(IV) *Hexafluorophosphate*, (XXII).—This was prepared from pyridine (1.0 mmol) and complex (XVII) (1.0 mmol) according to Clark and Mazer [12] as white needles (69%) (Found: C, 28.5; H, 4.0. $C_{18}H_{30}As_2F_6NPPt$ requires C, 28.8; H, 3.9). ^{1}H N.m.r. spectrum ($CDCl_3$): δ 0.48 [3 H, s, *J*(Pt–H), 78, *trans*-Pt–CH_3), 1.22 [6 H, s, *J*-(Pt–H), 60, *cis*-Pt–CH_3], 1.51 [6 H, s, *J*(Pt–H) 8, As–CH_3], and 1.70 p.p.m. [6 H, s, *J*(Pt–H) 10 Hz, As–CH_3].

fac-*Trimethyl*[racemic-o-*phenylenebis(methylphenylarsine)*]*pyridineplatinum*(IV) *Hexafluorophosphate*, (XXIII).—This complex was prepared as above, recrystallisation from dichloromethane–diethyl ether giving white needles (72%) (Found: C, 38.2; H, 3.9. $C_{28}H_{34}As_2NPPt$ requires C, 38.4; H, 3.8%). ^{1}H N.m.r. spectrum ($CDCl_3$): δ 0.31 [3 H, s, *J*(Pt–H) 76, *cis*-Pt–CH_3], 1.14 [3 H, s, *J*(Pt–H) 6, *trans*-Pt–CH_3], 1.28 [3 H, s, *J*(Pt–H) 64, *trans*-Pt–CH_3], 1.89 [3 H, s, *J*(Pt–H), 8, As–CH_3], and 2.02 p.p.m. [3 H, s, *J*(Pt–H) 8 Hz, As–CH_3].

fac-*Trimethyl*[meso-o-*phenylenebis(methylphenylarsine)*]-*pyridineplatinum*(IV) *Hexafluorophosphate*, (XXIVa) *and* (XXIVb).—The two isomers (XIXa) and (XIXb) were treated separately with py and silver hexafluorophosphate in acetone as already described. Complex (XIXa) gave white plates of the hexafluorophosphate (XXIVa) (83%) (Found: C, 38.6; H, 4.1. $C_{28}H_{34}As_2F_6PPt$ requires C, 38.4; H, 3.8%). ^{1}H N.m.r. spectrum ($CDCl_3$): δ 0.63 [3 H, s, *J*(Pt–H) 76, *trans*-Pt–CH_3], 1.22 [6 H, s, *J*(Pt–H) 64, *cis*-Pt–CH_3], and 1.83 p.p.m. [6 H, s, *J*(Pt–H) 10 Hz, As–CH_3]. Complex (XIXb) gave white cubes of the hexafluorophosphate (XXIVb) (62%) (Found: C, 83.3; H, 4.0. $C_{28}H_{34}As_2F_6$-NPPt requires C, 38.4; H, 3.8%). ^{1}H N.m.r. spectrum ($CDCl_3$): δ −0.05 [3 H, s, *J*(Pt–H) 75, *trans*-Pt–CH_3], 1.36 [6 H, s, *J*(Pt–H) 62, *cis*-Pt–CH$_3$], and 2.04 p.p.m. [6 H, s, *J*(Pt–H) 8 Hz, As–CH_3].

o-*Phenylenebis(methylarsine)*, (XXVII), *from* o-*Phenylene-diarsine*, (XXVI).—Compound (XXVII) was prepared by the procedure of Carlton and Cook [21] although (XXVI) was prepared by Li[AlH_4] reduction of *trans*-1,3-dichloro-1,3-dihydro-2,1,3-benzoxadiarsole, (XXV),[13] rather than by the reduction of *o*-phenylenebis(dichloroarsine). The *arsine* (XXVII) (66%) was obtained as a colourless liquid, b.p. 93 °C (2.5 mmHg). The ^{1}H n.m.r. spectrum of this oil was the same as that reported [21] and showed an equal mixture of the *meso*- and *racemic*-isomers.

Reaction of Compound (XXVII) *with n-Butyl-lithium followed by Bromobenzene.*—A solution of (XXVII) (12.9 g, 0.05 mol) in thf (100 cm^3) was reacted with n-butyl-lithium (1.2M, 82.5 cm^3) dissolved in hexane at 0 °C. The solution was allowed to warm to room temperature and a solution of bromobenzene (15.7 g, 0.1 mol) in diethyl ether (100 cm^3) added dropwise. Evaporation of the solvent yielded a solid which was extracted with dichloromethane, filtered, and evaporated to dryness. Distillation of the residue gave an oil, b.p. 188—194 °C (0.05 mmHg) (18.6 g, 91%), shown by ^{1}H n.m.r. spectroscopy to consist of an equal mixture of the diastereoisomers (Ia) and (Ib).

o-*Phenylenebis(bromomethylarsine)*, (XXIX).—To a stirred solution of (II) (57.2 g, 0.2 mol) in carbon tetrachloride (200 cm^3) at 0 °C was added slowly a solution of bromine (64 g, 0.8 mol) in carbon tetrachloride (500 cm^3). A pale yellow granular solid precipitated (120 g) and was collected and dried *in vacuo*. The oxidation product, o-*phenylenebis-(dibromodimethylarsine)* (XXVIII), was found to be very sensitive to moisture and a satisfactory analysis was not obtained. The solid (XXVIII) was heated *in vacuo* until evolution of bromomethane had ceased and a deep red oil remained. The oil was then distilled and gave three fractions: (*i*), a colourless liquid, b.p. 34—40 °C (1 mmHg) (4 g, 0.008 mol, 0.5%), *dibromomethylarsine*, δ (in CCl_4) 2.61 p.p.m. (s, As–CH_3), *m/e* 248, 250, and 252 ($MeAsBr_2$); (*ii*), a yellow liquid, b.p. 80—90 °C (0.7 mmHg) (6 g, 0.025 mol, 6%), *bromomethylphenylarsine*, δ (in CCl_4) 1.97 (3 H, s, As–CH_3) and 7.75 p.p.m. (5 H, m, aromatics), *m/e* 246 and 248 [PhAs(Br)Me]; and (*iii*), a pale yellow solid, b.p. 160—180 °C (0.5 mmHg) (63 g, 0.15 mol, 76%), o-*phenylenebis(bromo-methylarsine)* (XXIX) (Found: C, 22.9; H, 2.2. $C_8H_{10}As_2$-Br_2 requires C, 23.0; H, 2.4%), δ (in $CDCl_3$) 2.08 (6 H, s, As–CH_3) and 7.86 p.p.m. (4 H, AA′BB′, aromatics). Attempted crystallisation of (XXIX) from carbon tetrachloride gave white crystals, m.p. 162—163 °C (Found: C, 18.0; H, 1.2. $C_6H_4As_2Br_2O$ requires C, 17.9; H, 0.9%). ^{1}H N.m.r. spectrum ($CDCl_3$): δ 7.93 p.p.m. (complex m, aromatics). Mass spectrum: *m/e* 400, 402, and 404. This solid was assigned as 1,3-*dibromo*-1,3-*dihydro*-2,1,3-*benzoxa-diarsole*, (XXX).

Attempted Racemisation of Compound (XXIX) *using Hydrobromic Acid.*—Compound (XXIX) (2 g, 5 mmol) was dissolved in ethanol (20 cm^3) and concentrated HBr (49%, 10 cm^3) added. The mixture was heated under reflux for 18 h, evaporated to dryness using a rotary evaporator, the residue extracted into dichloromethane, dried ($MgSO_4$), and the dichloromethane removed. An examination of the ^{1}H n.m.r. spectrum of the residue oil (1.6 g) showed the presence of only the original diastereoisomer with one sharp As–CH_3 resonance at δ 2.08 p.p.m.

Reduction of Compound (XXIX) *with* Li[AlH_4].—A solution of (XXIX) (4.2 g, 0.01 mol) in benzene (100 cm^3) was added with stirring to a suspension of Li[AlH_4] (0.5 g, 0.01 mol) in diethyl ether (150 cm^3) during the course of 0.5 h. After the addition was complete the reaction mixture was heated under reflux for 1 h, cooled, water added, and the aqueous layer separated. The ether extract was dried ($MgSO_4$), evaporated to dryness, and the pale yellow oil distilled to give (XXVII) as a colourless liquid, b.p. 105 °C (5 mmHg) (1.9 g, 0.007 mol, 73%) (Found: C, 37.8; H, 4.9. $C_8H_{12}As_2$ requires C, 37.2; H, 4.6%). The ^{1}H n.m.r. spectrum showed a doublet centred at δ 1.20 p.p.m. and assigned to the As–CH_3 protons (*J* 6.8 Hz) which was not resolved further using a sweep width of 2 Hz cm^{-1} at 90 MHz.

Reaction of Compound (XXIX) *with Phenylmagnesium Bromide.*—Phenylmagnesium bromide, prepared from bromobenzene (3.1 g, 20 mmol) and magnesium (0.49 g, 20 mmol) in diethyl ether (150 cm^3), was added to a stirred solution of (XXIX) (2.1 g, 5.1 mmol) in benzene (50 cm^3). The reaction mixture was heated under reflux for 2 h, cooled, hydrolysed with water, and the organic layer separated and

dried ($MgSO_4$). Evaporation of the solvent and distillation of the residue gave an equal mixture of (Ia) and (Ib) as a pale yellow oil, b.p. 190—191 °C (0.05 mmHg) (1.6 g, 4.0 mmol, 76%).

Reaction of Compound (XXIX) *with Phenyl-lithium.*—Compound (XXIX) (2.1 g, 5.1 mmol) was dissolved in benzene (50 cm^3) and a solution of phenyl-lithium prepared from bromobenzene (3.1 g, 20 mmol) and finely divided lithium (0.28 g, 40 mmol) in diethyl ether (150 cm^3) added at room temperature. The reaction mixture was then heated under reflux for 1 h, cooled, hydrolysed with water, and the organic layer separated and dried ($MgSO_4$). The solvent was removed to yield a pale yellow oil which on distillation gave an equal mixture of (Ia) and (Ib) as a pale yellow oil, b.p. 184—186 °C (0.05 mmHg) (1.46 g, 3.5 mmol, 69%).

o-*Phenylenebis(iodomethylarsine)*, (XXXI).—Compound (XXIX) (20 g, 0.048 mol) was dissolved in acetone (200 cm^3) and treated with an excess of KI dissolved in acetone. The solvent was removed and the residue extracted with dichloromethane, evaporated to dryness, and the yellow solid remaining recrystallised from carbon tetrachloride to give (XXXI) as large yellow cubes, m.p. 84—84.5 °C (24 g, 0.047 mol, 98%) (Found: C, 18.8; H, 1.9; As, 29.3. $C_8H_{10}As_2I_2$ requires C, 18.8; H, 1.9; As, 29.4%). ^1H N.m.r. spectrum ($CDCl_3$): δ 2.20 (6 H, s, As–CH_3) and 7.61 p.p.m. (4 H, AA'BB', aromatics). Mass spectrum: *m/e* 510 (3%, $C_8H_{10}As_2I_2$).

Reaction of Compound (XXXI) *with Sodium followed by Bromobenzene.*—A solution of (XXXI) (10.2 g, 0.02 mol) in thf (200 cm^3) was added slowly to a stirred suspension of sodium (2.3 g, 0.1 mol) in thf (100 cm^3) cooled in an ice-bath. The reaction mixture was stirred for an additional hour and bromobenzene (6.2 g, 0.04 mol) then slowly added to the cooled solution. After the reaction was over, water (50 cm^{-3}) and then diethyl ether (100 cm^3) was added and the organic layer separated and dried ($MgSO_4$). Evaporation of the solvent and distillation of the residue gave an equal mixture of (Ia) and (Ib) as a pale yellow oil, b.p. 184—187 °C (0.05 mmHg) (2.78 g, 0.007 mol, 34%).

Reaction of Compound (XXVII) *with Carbon Tetrachloride.*—(*a*). Treatment of compound (XXVII) (1.3 g, 5 mmol), obtained from reaction of n-butyl-lithium, iodomethane, and (XXVI), with carbon tetrachloride (10 cm^3) at room temperature for 18 h gave a quantitative yield of *o*-phenylenebis(chloromethylarsine), (XXXII), and chloroform was eliminated. Distillation of the (XXXII) gave a colourless liquid, b.p. 120—122 °C (0.5 mmHg) (Found: C, 34.6; H, 2.0. $C_8H_{10}As_2Cl_2$ requires C, 34.4; H, 2.3%). Mass spectrum: *m/e* 348 and 350. The ^1H n.m.r. spectrum of (XXXII) obtained by this method showed *two* As–CH_3 singlets at δ 1.93 and 1.99 p.p.m. indicating a mixture of the *meso*- and *racemic*-isomers.

(*b*). Similar treatment of (XXVII), obtained by reduction of (XXIX), with carbon tetrachloride at room temperature for 18 h gave, after work-up and distillation, (XXXII) (92%) (Found: C, 34.1; H, 2.0. $C_{10}H_8As_2Cl_2$ requires C, 34.4; H, 2.3%). The mass spectrum of this product was identical to that found above. The ^1H n.m.r. spectrum, however, showed *one* As–CH_3 singlet at δ 1.93 p.p.m. which indicated that only one of the two possible diastereoisomers was present.

1,3-*Dihydro*-1,3-*dimethyl*-2,1,3-*benzoxadiarsole*, (XXXIII).—(*a*). A solution of NaOH (4 g, 0.1 mol) in water (10 cm^3) was added to (XXIX) (0.52 g, 0.0125 mol) and the mixture was boiled for 3 h. The oily product which separated on cooling was extracted into diethyl ether and the solution dried ($MgSO_4$). The solvent was removed from the extract under reduced pressure and the residue distilled to give (XXXIII) as a colourless *liquid*, b.p. 120—122 °C (0.5 mmHg) (0.250 g, 75 mmol, 61%) (Found: C, 35.7; H, 3.6. $C_8H_{10}As_2O$ requires C, 35.3; H, 3.7%). ^1H N.m.r. spectrum ($CDCl_3$): δ 1.43 (6 H, s, As–CH_3), and 7.58 p.p.m. (4 H, complex m, aromatics). Mass spectrum: *m/e* 272 (42%, $C_8H_{10}As_2O$).

(*b*). Treatment of (XXIX) (0.52 g, 1.25 mmol) with a solution of sodium cyanide (125 mg, 2.5 mmol) in acetone (10 cm^3) at room temperature for 4 h gave, after filtration and distillation, (XXXIII) as a colourless liquid, b.p. 122—126 °C (0.5 mmHg) (0.26 g, 0.96 mmol, 75.8%) (Found: C, 35.7; H, 3.9%). The ^1H n.m.r. and mass spectra were identical to those described above.

Reaction of Compound (XXXIII) *with Thionyl Chloride.*—A solution of (XXXIII) (1.4 g, 0.005 mol) in carbon tetrachloride (3.3 g) was cooled to 0 °C and thionyl chloride (3.3 g) was added dropwise. The solution was then distilled and gave (XXXII), b.p. 118—120 °C (0.5 mmHg) (1.4 g, 85%) (Found: C, 29.2; H, 3.0%). ^1H N.m.r. spectrum (CCl_4): δ 1.93 (6 H, s, As–CH_3) and 7.62 p.p.m. (4 H, AA'BB', aromatics).

Reaction of Compound (XXIX) *with Diethylamine and Hydrogen Chloride.*—Compound (XXIX) (2.08 g, 0.005 mol) was dissolved in light petroleum (200 cm^3), the reaction mixture cooled to −30 °C in a bath of solid CO_2–ethanol, and diethylamine (1.46 g, 0.02 mol) in light petroleum (200 cm^3) added dropwise to the cooled solution. The reaction mixture was warmed to room temperature, heated under reflux for a few minutes, and then cooled again to room temperature and filtered. The solvent was removed by distillation under reduced pressure to leave o-*phenylenebis(diethylaminomethylarsine)*, (XXXIV), as an oil (1.8 g). Attempted distillation of the oil resulted in decomposition. ^1H N.m.r. (CCl_4): δ 1.06 (12 H, br t, *J* 7 Hz, N–CH_2–CH_3), 1.42 (6 H, s, As–CH_3), 2.90 (8 H, br m, N–CH_2–CH_3), and 7.50 p.p.m. (4 H, complex m, aromatics). Mass spectrum: *m/e* 400 ($C_{16}H_{30}As_2N_2$). The oil was dissolved in diethyl ether (200 cm^3) and treated with gaseous hydrogen chloride for 0.5 h. White diethylammonium chloride precipitated during the course of the reaction. The solution was filtered and the colourless filtrate evaporated to leave an oil which on distillation gave (XXXII), b.p. 120—125 °C (0.5 mmHg) (0.81 g, 0.0024 mol, 50%) (Found: C, 30.0; H, 3.0%). ^1H N.m.r. spectra (CCl_4): δ 1.93 p.p.m. (s, As–CH_3).

Resolution of Compound (Ib).—To a solution of (XVb) (11.6 g, 0.05 mol) in methanol (100 cm^3) was added a solution of sodium D(−)-dibenzoylhydrogentartrate,[32] prepared from D(−)-dibenzoyltartaric acid monohydrate (8.3 g) and sodium carbonate (2.12 g) in water (100 cm^3). The mixture was heated on a steam-bath for 1 h to partly remove the methanol and then cooled and extracted with dichloromethane (3 × 50 cm^3). The combined extracts were dried ($MgSO_4$) and the solvent removed *in vacuo* to leave an oil containing the diastereoisomers (±)-benzyl(methyl)[(2-methylphenylarsinophenyl)]phenylarsonium D(−)-dibenzoylhydrogentartrate, (±)- and (=)-(XXXV) (15.1 g). These were dissolved in hot isopropyl alcohol (150 cm^3) and the solution left overnight at 0 °C whereupon white crystals of (+)-benzyl(methyl)[(2-methylphenylarsino)phenyl]-phenylarsonium D(−)-dibenzoylhydrogentartrate, (XXXV),

[32] D. M. Coyne, W. E. McEwan, and C. A. Vander-Werf, *J. Amer. Chem. Soc.*, 1956, **78**, 3061.

were obtained (6.9 g), m.p. 123—125 °C, α(293.15 K, 589.3 nm) −21.1° (MeOH, c, 10.01 g l^{-1}) (Found: C, 57.85; H, 5.65. $C_{45}H_{40}As_2O_8 \cdot 4H_2O$ requires C, 58.0; H, 5.2%). The salt (±)-(XXXV) was dissolved in acetone and added to a solution of excess of aqueous KPF_6 to precipitate the (+)-arsonium hexafluorophosphate, (XXXVI). Recrystallisation of this compound from acetone–diethyl ether gave white needles of the pure product, m.p. 186—188 °C, α(293.15 K, 589.3 nm) + 3.1° (acetone, c, 10.10 g l^{-1}) (Found: C, 50.3; H, 4.3. $C_{27}H_{27}As_2F_6P$ requires C, 50.2; H, 4.2%).

The isopropyl alcohol filtrate from the initial separation was concentrated (*ca.* 50 cm^3) and carefully diluted with diethyl ether to induce crystallisation of the white (−)-arsonium D(−)-dibenzoylhydrogentartrate, (=)-(XXXV). This was collected (4.1 g) and then recrystallised from hot Dimethyldigol (30 cm^3); slow cooling gave the pure diastereoisomer (=)-(XXXV), m.p. 118—120 °C, α(293.15 K, 589.3 nm) −73.6° (MeOH, c, 10.06 g l^{-1}) (Found: C, 58.4; H, 5.4. $C_{45}H_{48}As_2O_8 \cdot 4H_2O$ requires C, 58.0; H, 5.2%). Treatment of this diastereoisomer with KPF_6 by the same procedure described above yielded the (−)-arsonium hexafluorophosphate (XXXVI) as white needles, m.p. 184—185 °C, α(293.15 K, 589.3 nm) −2.8° (acetone, c, 10.11 g l^{-1}) (Found: C, 50.5; H, 4.3. $C_{27}H_{27}As_2F_6P$ requires C, 50.2; H, 4.2%).

(+)-o-*Phenylenebis(methylphenylarsine)*, (Ib).—A suspension of (XXXVI) (6.4 g) in thf (100 cm^3) was added to a stirred suspension of $LiAlH_4$ (3.8 g) in thf (50 cm^3) and the mixture heated under reflux for 6 h. The usual aqueous work-up and a recrystallisation of the crude product from ethanol gave pure (+)-*o*-phenylenebis(methylphenylarsine), (Ib) (3.6 g, 88%) as white needles, m.p. 91 °C, α(293.15 K, 589.3 nm) +31.4° ($CHCl_3$, c, 10.21 g l^{-1}) (Found: C, 58.4; H, 5.0. $C_{20}H_{20}As_2$ requires C, 58.5; H, 4.9%). The ^1H n.m.r. and mass spectra of (+)-(Ib) were identical to those obtained for *racemic*-(Ib). Further recrystallisation of the sample did not alter the rotation

(−)-o-*Phenylenebis(methylphenylarsine)*, (Ib).—Reduction of (XXXVI) using the procedure described above yielded (−)-*o*-phenylenebis(methylphenylarsine), (Ib) (83%), as white cubes, m.p. 89 °C, α(293.15 K, 589.3 nm) −24.6° ($CHCl_3$, c, 10.08 g l^{-1}) (Found: C, 58.2; H, 5.3. $C_{20}H_{20}As_2$ requires C, 58.5; H, 4.9%). The ^1H n.m.r. and mass spectra of this compound were identical to those obtained for *racemic*-(Ib) and further recrystallisation did not alter the rotation.

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