985. *The Structure and Properties of Certain Polycyclic Indolo- and Quinolino-derivatives. Part XV.*[1] *Derivatives of 1-Phenyl-4-piperidone and its Phosphorus and Arsenic Analogues.*

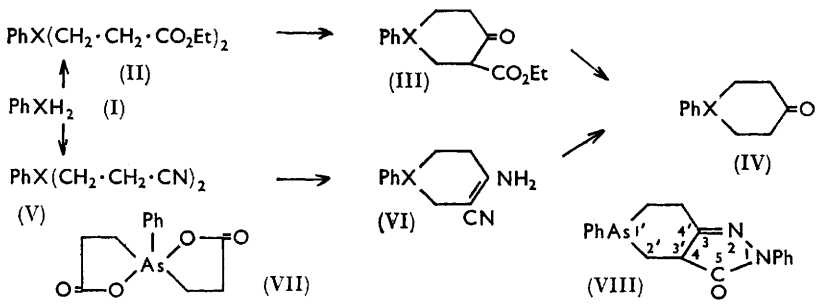
By M. J. Gallagher and Frederick G. Mann.

1-Phenyl-4-piperidone and 1-phenylarsacyclohexan-4-one have been synthesised, and the properties of these compounds and of the known 1-phenylphosphacyclohexan-4-one investigated.

The methiodides of the nitrogen and arsenic members, unlike that of the phosphorus member, form very stable 4,4-dimethyl ketals. The nitrogen, phosphorus, and arsenic members form unstable phenylhydrazones, but only that of the oxo-phosphine has been converted into the indolo-derivative. The three eutropic members condense with *o*-aminobenzaldehyde to give the corresponding quinolino-derivatives. These derivatives of the nitrogen and phosphorus members each form a series of hydrochlorides: the colour of certain of these salts has not yet been satisfactorily explained. The three members also condense with isatin in alkaline solution to give the 4′-carboxyquinolino-derivatives: these acids do not form zwitterions and cannot readily be decarboxylated.

In continuation of our studies on the application of the Fischer indolisation reaction and the Friedländer reaction to cyclic oxo-amines and analogous compounds, we have prepared the eutropic series, 1-phenyl-4-piperidone (IV; X = N), 4-oxo-1-phenylphosphacyclohexan-4-one (IV; X = P), and 1-phenylarsacyclohexan-4-one (IV; X = As).

In the nitrogen series, we find that aniline when heated with ethyl acrylate and cuprous chloride gave diethyl phenylimino-ββ′-dipropionate (II; X = N) in 66% yield with a forerun of ethyl β-anilinopropionate in 14% yield. Alternatively, when aniline was converted into *NN′*-bis-2-cyanoethylaniline (V; X = N) and then by alkaline hydrolysis into phenylimino-ββ′-dipropionic acid,[2] esterification of the latter with ethanol and hydrogen chloride gave these esters in 9 and 40% yield, respectively. The former method is preferable also to the use of ethyl β-bromopropionate to convert aniline in two stages into the ethyl and then the diethyl ester.[3]



The diethyl ester (II; X = N), when heated with sodium in xylene, afforded the piperidone ester (III; X = N),[3,4] which on acid hydrolysis gave 1-phenyl-4-piperidone (IV; X = N). This compound had normal ketonic properties, forming a crystalline 2,4-dinitrophenylhydrazone, a 4-phenylsemicarbazone, and an unstable phenylhydrazone.

The dinitrile (V; X = N), when heated with sodium t-butoxide in xylene gave

[1] Part XIV, Braunholtz, Mallion, and Mann, *J.*, 1962, 4346.
[2] Cookson and Mann, *J.*, 1949, 67.
[3] Thayer and McElvain, *J. Amer. Chem. Soc.*, 1927, **49**, 2862.
[4] McElvain, *J. Amer. Chem. Soc.*, 1926, **48**, 2179.

4-amino-3-cyano-1,2,5,6-tetrahydro-1-phenylpyridine (VI; X = N), but this compound on acid hydrolysis did not afford the ketone (IV; X = N).

1-Phenylphosphacyclohexan-4-one (IV; X = P) was prepared by Welcher, Johnson, and Wystrach's method,[5] the dinitrile [6] (V; X = P) being converted by sodium t-butoxide in boiling toluene into the amino-nitrile (VI; X = P): acid hydrolysis then gave the oxo-phosphine (IV; X = P). This compound is a reasonably strong base, and forms a stable hydrochloride and hydrobromide.

We have extended the spectroscopic evidence adduced by the American authors [5] for the structure of the amino-nitrile (VI; X = P), and find that the nitrogen analogue (VI; X = N) also has this structure. The infrared spectrum of the nitrogen compound (VI; X = N) in a Nujol mull shows two sharp bands at 3450 and 3360 cm.$^{-1}$ characteristic of an NH_2 group, a third sharp band at 3250 cm.$^{-1}$, this being an NH_2 overtone band, and an NH_2 deformation band at 1645 cm.$^{-1}$: the spectrum of the phosphorus analogue (VI; X = P) shows four similar bands at 3400, 3330, 3240, and 1645 cm.$^{-1}$, respectively. If either of these compounds had the isomeric 4-imino-structure, the :NH group should have given only one band in the 3400—3300 cm.$^{-1}$ region.

The nuclear magnetic resonance spectra of these two compounds in chloroform solution confirm these structures, and give no evidence of a tautomeric mixture of isomers in solution. These spectra were obtained at 40 Mc./sec. by using a Perkin-Elmer spectrometer and permanent magnet with sample spinning: positions of references are quoted as chemical shifts on the τ scale (τ $SiMe_4$ = 10·00) and have been measured against tetramethylsilane as an internal reference. The spectrum of the compound (VI; X = N) reveals the NH_2 group as a broad band centred at 5·54; the methylene group in position 2 ($N{\cdot}CH_2{\cdot}C{:}C$) appears as a strong peak at 6·29, with slight shoulders at 6·14 and 6·21; that in position 5 ($CH_2{\cdot}C{:}C$) as a triplet of sharp bands, the strongest (central) at 7·72; and that in position 6 ($CH_2{\cdot}N$) as a similar triplet with the strongest band at 6·58. The spectrum of the compound (VI; X = P) also shows the NH_2 group as a rather broad peak at 5·68; the methylene peaks, which undergo some splitting by the phosphorus, are moved to higher values and the triplets partly overlap, but the sharp peaks at 7·45, 8·06, and 7·90 probably represent the above three CH_2 groups, respectively.

In the arsenic series, the dinitrile [7] (V; X = As) had been cyclised by the earlier workers [5] to the crystalline amino-nitrile (VI; X = As), but we isolated this compound only as an oil. Dr. Welcher kindly provided us with full details of this preparation, but in view of the lengthy procedure and low yield this route was abandoned as a practicable source of the oxo-arsine (IV; X = As).

The dinitrile was therefore hydrolysed to di-(2-carboxyethyl)phenylarsine, which with ethanol and hydrogen chloride afforded the diethyl ester (II; X = As) in 95% yield. In other syntheses, phenylarsine, $PhAsH_2$, when heated with ethyl acrylate and acetic acid, gave the ester (II; X = As) in 17% yield and much arsenobenzene; alternatively, the arsine when treated in liquid ammonia with one equivalent of sodium and then one of ethyl β-bromopropionate, with repetition of this treatment, gave the ester (II; X = As) in 29% yield.

The diethyl ester, when boiled with sodium ethoxide in benzene, afforded the crude oxo-ester (III; X = As) in 99% yield; acid hydrolysis then gave 1-phenyl-1-arsacyclohexan-4-one (IV; X = As) in 89% yield.

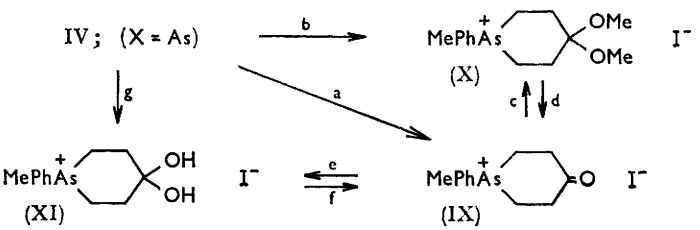
It is noteworthy that the diethyl ester (II; X = As) underwent hydrolysis and oxidation very slowly when exposed to damp air at room temperature, and rapidly in hot acetone–hydrogen peroxide, to form the spiro-dilactone (VII), previously prepared by the direct oxidation of di-(2-carboxyethyl)phenylarsine.[8] Furthermore, the oxo-ester

[5] Welcher, Johnson, and Wystrach, *J. Amer. Chem. Soc.*, 1960, **82**, 4437.
[6] Mann and Millar, *J.*, 1952, 4453.
[7] Cookson and Mann, *J.*, 1947, 618.
[8] Braunholtz and Mann, *J.*, 1957, 3285.

(III; X = As) with phenylhydrazine afforded the crystalline 5-oxo-1,1′-diphenyl-1′-arsacyclohexano(4′,3′-3,4)-2-pyrazoline (VIII), whereas the oxo-ester (III; X = N) similarly treated gave only tars.

The piperidone (IV; X = N) and its arsenic analogue (IV; X = As) show on quaternisation one unusual feature which is not shared by the phosphorus analogue (IV; X = P). The products in the arsenic series have been most fully investigated and are discussed here.

The oxo-arsine (IV; X = As) when heated with methyl iodide gave the colourless crystalline methiodide (IX), the infrared spectrum of which showed a strong C=O band at 1700 cm.$^{-1}$. When however, the oxo-arsine was heated with methanolic methyl iodide, the crystalline 4,4-dimethoxy-1-phenyl-1-arsacyclohexane methiodide (X) was formed, and was purified by crystallisation from ethanol. This structure is based on the following evidence. (i) The analyses of the iodide (X) and the corresponding picrate are correct, and the iodide is stable to heat (1 hr. at 60°/0·1 mm.). (ii) The infrared spectrum shows no C=O or OH absorption, and the compound cannot therefore be the ethanolate of the



a, MeI. b, MeOH–MeI. c, MeOH + trace HI. d, Aq. HI. e, Aq. MeCO–Et_2O. f, Recryst. from EtOH. g, EtOH–MeI.

iodide (IX). Further, this spectrum shows a strong doublet at 1107 and 1057 cm.$^{-1}$: Tschamler and Leutner [9,10] have recorded a strong doublet in the 1150—1080 cm.$^{-1}$ region, characteristic of the C·O·C·O·C grouping. (iii) Nuclear magnetic resonance spectra, obtained as described above, showed a strong peak at τ 3·03 due to the aromatic protons, a single sharp peak at τ 7·91 corresponding to the AsMe group, and a split peak at τ 6·98 and 7·00 corresponding to the methoxyl groups (split because one MeO group is closer than the other to the aromatic ring), and the methylene protons of the arsacyclohexane ring appear as a complex of five peaks between 7·3 and 8·0, the expected sixth band being obscured by the AsMe band. (iv) The dimethoxy-salt (X) was also readily formed when the methiodide (IX) was boiled in methanol containing a trace of hydriodic acid, but the oxo-arsine (IV; X = As) when similarly treated was unaffected. The salt (X) was also readily hydrolysed by boiling aqueous hydriodic acid to give a crude product which on recrystallisation from ethanol gave the methiodide (IX).

The methiodide (IX) when recrystallised from aqueous acetone–ether gave an apparent monohydrate; this compound is, however, almost certainly the 4,4-dihydroxy-salt (XI), for its infrared spectrum shows only weak carbonyl absorption but a strong doublet at 1087 and 1055 cm.$^{-1}$, which falls within the region of OH deformation vibrations; the normal OH stretching absorption appears as a sharp band at 3340 cm.$^{-1}$. This compound, although possessing marked thermal stability, re-formed the oxo-salt (IX) on repeated recrystallisation from absolute ethanol.

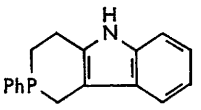
The formation of such ketal salts is possibly limited to the dimethoxy-member (IX). The oxo-arsine, when boiled in ethanolic methyl iodide, afforded only the crude dihydroxy-salt (XI) and thence by recrystallisation from ethanol the methiodide (IX); further, when an ethanolic solution of the pure methiodide (IX), containing a trace of hydriodic acid, was boiled, only the dihydroxy-salt (XI) was isolated.

[9] Tschamler and Leutner, *Monatsh.*, 1952, **83**, 1502.
[10] Tschamler, *Spectrochim. Acta*, 1953, **6**, 95.

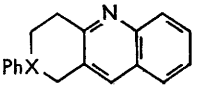
The piperidone (IV; X = N) with boiling methanolic methyl iodide gave the 4,4-dimethoxy-methiodide (as X), which showed no infrared carbonyl absorption; with boiling methyl iodide, with or without ethanol, the piperidone gave an oily methiodide, which with aqueous acetone–ether gave the crystalline 4,4-dihydroxy-methiodide (as XI).

The oxo-phosphine (IV; X = P) in marked contrast gave solely the crystalline methiodide (as IX) under all the above conditions.

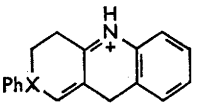
The three ketones (IV; X = N, P, As) form very unstable phenylhydrazones, whose behaviour on attempted indolisation again illustrates the difference between the phosphorus member and the other two members. 1-Phenyl-4-piperidone phenylhydrazone gave only intractable tars when warmed with ethanolic hydrogen chloride, acetic acid, dilute sulphuric acid, zinc chloride, or boron trifluoride. This contrasts with the unstable 1-methyl-4-piperidone phenylhydrazone, which with hot dilute sulphuric acid gives 2,3,4,5-tetrahydro-4-methyl-4-carboline.[11] The phenylhydrazone of the oxo-arsine (IV; X = As) also gave tars under all conditions for cyclisation investigated, but that of the oxo-phosphine (IV; X = P) with ethanolic hydrogen chloride gave the pale yellow tricyclic compound (XII), the structure of which was shown by an NH band at 3470 cm.$^{-1}$ in its infrared spectrum. The oxo-phosphine thus differs markedly from tetrahydro-1-phenyl- and -1-methyl-4-oxoquinolines, and other similar amino-ketones, whose phenylhydrazones give ψ-indoles with ethanolic hydrogen chloride.[2,12]



(XII)



(XIII)



(XIV)

The Friedländer Reaction.—The three ketones (IV; X = N, P, or As) react similarly with alkaline *o*-aminobenzaldehyde, the first, for example, giving the benzonaphthyridine (XIII; X = N). The structure of this compound was confirmed by its nuclear magnetic resonance spectrum (40 Mc./sec.; Varian Associates V4300B spectrometer; 12″ electromagnet; flux stabilisation; τ $SiMe_4$ = 10; measured against t-butyl alcohol as internal reference). The spectrum showed three peaks at τ 3·17 (aromatic C–H), 7·12 (N·CH_2·CH_2·Ar), and 8·09 (N·CH_2·C), respectively. The peak at τ 7·12, which has approximately twice the area of that at 8·09, appears as a single peak presumably because the coupling constant is zero or is too small to permit resolution. The corresponding spectrum of the base (XIII; X = P) is considerably more complex owing to the presence of the magnetic phosphorus nucleus and is not capable of simple interpretation. That the three bases (XIII; X = N, P, and As) have essentially the same structure is shown, however, by their almost identical ultraviolet absorption spectra in ethanolic solution.

Of the three bases (XIII; X = N, P, or As), the arsenic member has only one basic group and gives a colourless monohydrochloride, whereas the nitrogen and phosphorus members have two basic centres; the structure and colour of their salts present some curious features.

When the piperidine derivative (XIII; X = N) in ethanolic solution is treated with

$$\text{(XIII; X = N)} \xrightarrow{HCl} \text{(XIII; X = N),2HCl,2H}_2\text{O} \underset{HCl}{\overset{H_2O}{\rightleftharpoons}} \text{(XIII; X = N),HCl,2H}_2\text{O} \rightleftharpoons \text{(XIII; X = N),HCl}$$

hydrogen chloride, an unstable hydrochloride separates, which on recrystallisation from dilute hydrochloric acid affords the stable yellow dihydrochloride dihydrate. The latter salt, when recrystallised from water, gives a red monohydrochloride dihydrate, which when heated under reduced pressure gives an anhydrous orange-red hydrochloride; this

[11] Cook and Reid, *J.*, 1945, 399.
[12] Mann, *J.*, 1949, 2816; Braunholtz and Mann, *J.*, 1955, 381; Mann and Smith, *J.*, 1951, 1898; Almond and Mann, *J.*, 1952, 1870.

on exposure to air rapidly reverts to the dihydrated form. All these salts on basification afford the base (XIII; X = N).

Similar relationships hold in the phosphorus series, although colour formation is weaker. The colourless base (XIII; X = P) gives a colourless dihydrochloride dihydrate, a yellow monohydrochloride dihydrate, and a pale cream-coloured anhydrous monohydrochloride.

The cause of the colour of the dihydrochloride dihydrate in the piperidine series, and the marked intensification in colour which in each series accompanies the conversion of this salt into the monohydrochloride dihydrate, are difficult to explain. Clearly, simple monoprotonation of the compounds (XIII; X = N or P) could not give a coloured cation of the cyanine salt type. Braunholtz and Mann [12] have shown that in related systems, for example, the red 1,2-dihydro-1-methylquinolino(3,4-3′,2′)quinoline monohydrochloride, in boiling hydrochloric acid solution undergoes an allylic rearrangement to the

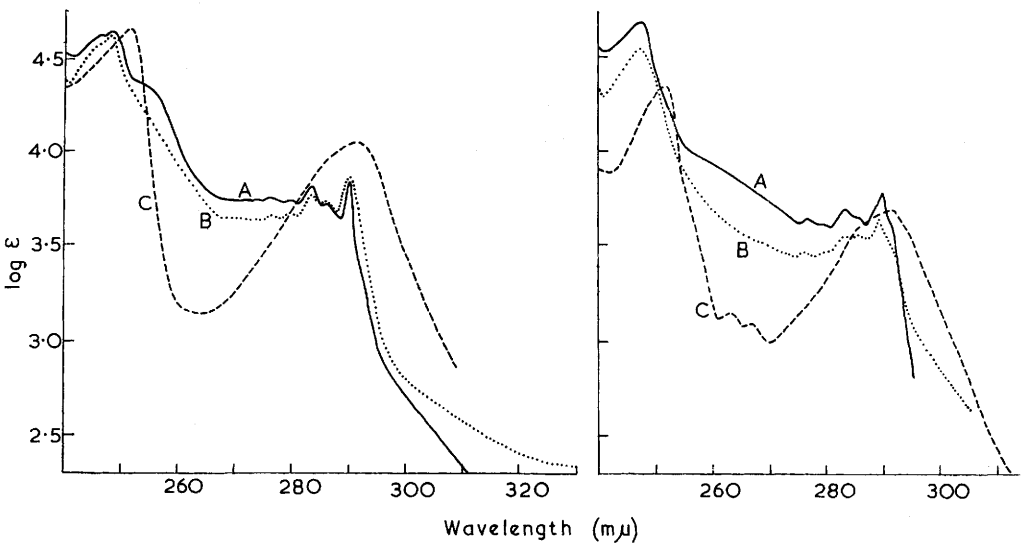


FIG. 1.

FIG. 2.

FIG. 1. Ultraviolet spectra of: A, the base (XIII; X = N), 2·486 mg. in 100 c.c. of ethanol; B, its monohydrochloride, 2·601 mg. in 100 c.c. of ethanol; C, its dihydrochloride, 2·202 mg. in 100 of c.c. ethanol containing 1 c.c. of conc. HCl.

FIG. 2. Ultraviolet spectra of: A, the base (XIII; X = P), 2·064 mg. in 100 c.c. of ethanol; B, its monohydrochloride, 2·292 mg. in 100 c.c. of ethanol; C, its dihydrochloride, 3·780 mg. in 100 c.c. of ethanol containing 1 c.c. of conc. HCl.

isomeric buff-coloured monohydrochloride. If the bases (XIII; X = N or P) were exceptionally sensitive to this isomerisation even in the presence of cold dilute acids to give the cation (XIV; X = N or P), the monohydrochlorides might be coloured. In all previous cases, however, vigorous conditions were required to effect this isomerism to the salts, and the " allylic " base itself was always thermally less stable than the normal base.

The bases (XIII) or the cations (XIV) should give colourless dihydrochlorides, which is not true for the piperidine series (XIII; X = N).

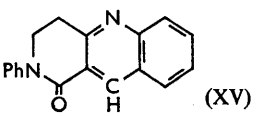
The ultraviolet spectra appear to show clearly that the monohydrochloride in each series cannot have the markedly different structure (XIV), for in the nitrogen series (XIII; X = N) the spectra of the base and its monohydrochloride in ethanol are closely similar, whereas that of the dihydrochloride has only a general resemblance to that of the base (Fig. 1): the same relationships hold in the phosphorus series (XIII; X = P) (Fig. 2). These results were not influenced by dissociation of the salts in the very dilute solutions

employed: the solutions of the monohydrochlorides retained a marked yellow colour, whereas hydrochloric acid was added to those of the dihydrochlorides to suppress their more ready dissociation to the monohydrochlorides.

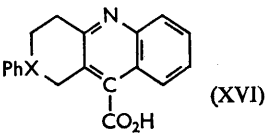
It should be noted that the only significant difference between the spectrum of the base (XIII; X = N) and its monohydrochloride is that the latter shows a small but steadily greater absorption from 340 to 400 mμ (Fig. 1), which undoubtedly corresponds to the orange-red colour of the salt. Furthermore, over the range 200—340 mμ, the difference between the spectrum of the base (or its monohydrochloride) and that of the dihydrochloride is closely similar in type to the difference between the spectra of quinoline and its hydrochloride, which suggests that protonation of the base occurs first on the PhN: group and, secondly, on the quinoline-nitrogen atom.

Certain diamines which give salts whose marked colour cannot be explained by classical or resonance structural theories have been discussed by Murrell,[13] who has suggested an explanation for the colour based on molecular-orbital considerations. It is, however, very difficult to apply these considerations to our monohydrochlorides, particularly in view of the methylene groups separating the two basic centres, and they cannot apparently be applied to the coloured dihydrochloride of the base (XIII; X = N). The cause of the colours in these salts therefore remains obscure.

The base (XIII; X = N) when treated in cold acetone solution with potassium permanganate underwent oxidation to the amide (XV). Allocation of the oxo-group to position 2 is based on the infrared spectrum, which showed a strong band at 1650 cm.$^{-1}$, attributed to an amide C=O group, and also on analogy with the ready atmospheric oxidation of 1,2-dihydro-1-phenyl(and methyl)quinolino(3,4-3′,2′)quinoline, in which the CH_2 group, similarly situated between the RN and the 4′-CH group, is converted into a CO group.[12,13] Similar experiments with the bases (XIII; X = P or As) were not undertaken owing to the ready oxidation of the tertiary phosphine (arsine) group.



(XV)



(XVI)

The Pfitzinger Reaction.—The three ketones (IV; X = N, P, or As), when treated with isatin in boiling 80% aqueous-ethanolic potassium hydroxide, gave the corresponding crystalline acids (XVI; X = N, P, or As), of which the first was yellow and the second and third almost colourless. The acid (XVI; X = N) was readily oxidised in air, but no definite compound could be isolated from the brown product; the acid could not be sublimed under reduced pressure. The phosphorus and arsenic acids were stable when exposed to the air, and could readily be sublimed. Many similar Pfitzinger acids prepared in this series, such as 1,2-dihydro-1-methyl(or phenyl)quinolino(3,4-2′,3′)quinoline-4′-carboxylic acid,[12] existed as deep red zwitterions, but all such acids had a second nitrogen atom which is effectively conjugated to the quinoline-2′-nitrogen atom and hence able to share the positive charge when the latter atom was protonated: almost all these acids underwent decarboxylation on attempted sublimation. The acids (XVI; X = N, P, or As) show no evidence of zwitterion formation. Their infrared spectra show a broad band of low intensity centred at *ca.* 2000 cm.$^{-1}$ and attributable to strongly hydrogen-bonded OH groups, probably arising from intermolecular interaction of the CO_2H groups and the quinoline-nitrogen atoms. The three spectra show C=O absorption at 1645, 1625, and 1633 cm.$^{-1}$, respectively, these low values being also influenced by the above bonding. No evidence of the two strong bands at *ca.* 1580 and 1260 cm.$^{-1}$, characteristic of the CO_2^- ion, was detected.

[13] Murrell, *J.*, 1959, 296.

It is noteworthy that each of the acids (XVI; X = N or P) gave benzylthiouronium salts which existed in two forms having widely different melting points.

Experimental

All compounds were colourless unless otherwise described. Consistent m. p.s of certain compounds could be obtained only by the use of evacuated capillary tubes, noted as (E.T.); the temperature of immersion, if above room temperature, is denoted as (T.I.)

Diethyl Phenylimino-ββ′-dipropionate (II; X = N).—Interaction of aniline and ethyl acrylate without a catalyst gave solely ethyl β-anilinopropionate.[14] A mixture of aniline (30 g.), ethyl acrylate (100 g., 3 mol.), glacial acetic acid (48 g., 2 mol.), and cuprous chloride (6 g.) was heated under reflux with stirring under nitrogen for 20 hr. A solution of the cold product in ether (100 c.c.) was shaken with water (3 × 100 c.c.) and then with aqueous ammonia (*d* 0·880; diluted with an equal volume of water) (3 × 100 c.c.). The solvent was removed from the dried ethereal layer, and then unchanged aniline and ethyl acrylate by distillation at 15 mm. Careful fractionation of the residue gave ethyl β-anilinopropionate, b. p. 135—160°/0·6 mm. (7·5 g., 14%), and diethyl phenylimino-ββ′-dipropionate, b. p. 164—167°/0·6 mm., $n_D^{22.5}$ 1·514 (lit.,[3] 1·5176) (62·5 g., 66%).

A solution of di-(2-cyanoethyl)aniline (10 g.) in 50% aqueous ethanol (50 c.c.) containing potassium hydroxide (10 g.) was boiled under reflux for 8 hr., whereafter ammonia ceased to be evolved. The ethanol was distilled off, the residue was added to water (100 c.c.) chilled to 0°, and concentrated hydrochloric acid (14 c.c.) was added. The solution was extracted with ether (3 × 100 c.c.), and the dried extracts were distilled, the residual phenylimino-ββ′-dipropionic acid slowly solidifying; it had m. p. 110·5—111·5° (from ethyl acetate) (Found: C, 60·6; H, 6·3; N, 6·2. Calc. for $C_{12}H_{15}NO_4$: C, 60·8; H, 6·3; N, 5·9%). The pure acid, which was not hygroscopic as previously reported,[2] in subsequent preparations separated as crystals when the hydrochloric acid was added to the alkaline solution: the acid gave a benzylthiouronium salt, m. p. 146—146·5° (lit.,[2] 146°) (Found: N, 12·3. Calc. for $C_{28}H_{35}N_5O_4S_2$: N, 12·3%).

A solution of the acid (40 g.) in ethanol (300 c.c.) was saturated with hydrogen chloride whilst boiling under reflux for 3 hr. After removal of the ethanol, the cold oily residue was mixed with saturated sodium hydrogen carbonate solution (500 c.c.) and extracted with ether. Distillation of the dried extract afforded two fractions, (i) ethyl β-anilinopropionate, b. p. 104—107°/0·2 mm., n_D^{20} 1·531 (lit.,[3] 1·5315) (13·2 g., 40%) (Found: C, 68·0; H, 8·1; N, 7·5. Calc. for $C_{11}H_{15}NO_2$: C, 68·4; H, 7·8; N, 7·25%), and (ii) the crude diethyl ester (II; X = N), b. p. 107—142°/0·2 mm. (mainly 141—142°) (4·6 g., 9%).

Ethyl 4-Oxo-1-phenylpiperidine-3-carboxylate (III; X = N).—The pure diethyl ester (II; X = N) (43 g.) was cyclised by McElvain's method [3,4] to give the *ester* (III; X = N) in 57% yield. This crude ester resinified on attempted distillation: it was therefore converted into the pure hydrochloride, m. p. 146—147° (lit.,[3] 144—145°), liberated with aqueous potassium carbonate, and after extraction with ether obtained as a liquid, b. p. 140—141°/0·1 mm., n_D^{25} 1·562 (Found: C, 67·8; H, 6·8; N, 5·7. $C_{14}H_{17}NO_3$ requires C, 68·0; H, 6·9; N, 5·7%). The use of sodium ethoxide in place of sodium in the above cyclisation did not appreciably affect the yield.

1-*Phenyl-4-piperidone* (IV; X = N).—A solution of the keto-ester (III; X = N) (21·6 g.) in 20% hydrochloric acid (100 c.c.) was boiled under reflux for 1 hr., concentrated under reduced pressure to *ca.* 30 c.c., cooled, basified with 60% aqueous sodium hydroxide, and extracted with ether. Removal of the ether from the dried extract gave the crude *ketone* (IV; X = N) (12·7 g., 66%); when purified by recrystallisation from light petroleum (b. p. 40—60°) or (preferably) by distillation, it formed needles, m. p. 37—38°, b. p. 112°/0·5 mm. (Found: C, 75·4; H, 7·7; N, 8·1. $C_{11}H_{13}NO$ requires C, 75·4; H, 7·4; N, 8·0%).

It gave a 2,4-*dinitrophenylhydrazone*, red needles, m. p. 156—157°, from ethanol–benzene (1 : 1) (Found: C, 57·0; H, 4·4; N, 19·65. $C_{17}H_{17}N_5O_4$ requires C, 57·45; H, 4·8; N, 19·7%).

[14] Elderfield, Gensler, Bembry, Kremer, Brody, Hageman, and Head, *J. Amer. Chem. Soc.*, 1946, **68**, 1259.

Treatment with a solution of 4-phenylsemicarbazide in ethanol containing 10% acetic acid gave the 4-phenylsemicarbazone, m. p. 198—199° (lit.,[15] 199°) (Found: C, 69·9; H, 6·4; N, 18·8. Calc. for $C_{18}H_{20}N_4O$: C, 70·1; H, 6·5; N, 18·2%). The ketone gave a colourless phenylhydrazone, m. p. 92—93°, which even on rapid recrystallisation from light petroleum (b. p. 60—80°) gave a coloured product, m. p. 87—89°.

A solution of the ketone (IV; X = N) in methyl iodide was boiled under reflux for 1 hr. and the excess of iodide removed. The residual oil solidified and when crystallised from aqueous acetone–ether yielded *4,4-dihydroxy-1-phenylpiperidine methiodide*, m. p. 120—121° (Found: C, 43·2; H, 5·5; N, 4·4. $C_{12}H_{18}INO_2$ requires C, 43·0; H, 5·4; N, 4·2%). This product was also obtained when ethanolic methyl iodide was employed. When a solution of the ketone in methanolic methyl iodide was similarly treated, recrystallisation of the residue from ethanol–ether gave *4,4-dimethoxy-1-phenylpiperidine methiodide*, m. p. 162—163° (Found: C, 46·1; H, 6·0; N, 4·0. $C_{14}H_{22}IN_2O$ requires C, 46·3; H, 6·0; N, 3·9%).

4-Amino-3-cyano-1,2,5,6-tetrahydro-1-phenylpyridine (VI; X = N).—A solution of the dinitrile (V; X = N) (5 g.) in warm xylene (100 c.c.) was run into a stirred suspension of sodium t-butoxide [prepared from sodium (1 g.) and t-butyl alcohol (3·6 g.)] also in xylene (100 c.c.), which was then heated under reflux in nitrogen for 2·5 hr. The cold precipitated sodio-derivative, when collected and triturated with water, gave the *amino-compound* (VI; X = N) (3·4 g., 68%), needles, m. p. 140—141° (from benzene) (Found: C, 72·1; H, 6·35; N, 21·1. $C_{12}H_{13}N_3$ requires C, 72·4; H, 6·5; N, 21·1%). The hydrolysis of this compound with boiling 6N-hydrochloric acid for 11 hr. gave only a brown oil apparently devoid of ketonic properties.

1-Phenyl-1-phosphacyclohexan-4-one (IV; X = P).—Phenylphosphine was converted into di-(2-cyanoethyl)phenylphosphine (V; X = P) by Mann and Millar's method.[6] The distillation of the crude phosphine (V; X = P) afforded a forerun (14%) containing 2-cyanoethylphenylphosphine, for with methyl iodide it gave *2-cyanoethyldimethylphenylphosphonium iodide*, m. p. 171—172° (from ethanol) (Found: C, 41·3; H, 4·6; N, 4·0. $C_{11}H_{15}INP$ requires C, 41·4; H, 4·7; N, 4·3%). This salt did not affect the m. p. of another sample, m. p. 172—173°, prepared from 2-cyanoethylmethylphenylphosphine that was obtained by the interaction of sodium methoxide and di-(2-cyanoethyl)methylphenylphosphonium iodide.[16]

A sample of the phosphine (V; X = P), when hydrolysed by alkali and then acidified, gave an oil which when exposed in ethyl acetate solution to the air deposited *di-(2-carboxyethyl)-phenylphosphine oxide*, needles, m. p. 203—204°, from water (Found: C, 53·7; H, 6·0. $C_{12}H_{15}O_5P$ requires C, 53·3; H, 5·9%), $\nu_{max.}$ band at 1253s cm.$^{-1}$ (P : O).

The phosphine (V; X = P) was converted into the cyclic amino-compound [5] (VI; X = P) which on hydrolysis with boiling 6N-hydrochloric acid gave the ketone (IV; X = P) in 70% yield. The ketone gave a *hydrochloride dihydrate*, m. p. 231—233° (E.T., T.I., 220°) (Found: C, 50·2; H, 7·1. $C_{11}H_{14}ClOP,2H_2O$ requires C, 49·9; H, 6·8%); prolonged drying at 0·1 mm. gave the intensely hygroscopic *hydrochloride*, without change of m. p. (Found: C, 58·1; H, 6·6. $C_{11}H_{14}ClOP$ requires C, 57·8; H, 6·1%). The *hydrobromide dihydrate* had m. p. 240·5—241·5° (decomp.) (E.T., T.I., 230°) (Found: C, 42·9; H, 6·05. $C_{11}H_{14}BrOP,2H_2O$ requires C, 42·7; H, 5·8%).

A boiling solution of the ketone (IV; X = P) in methyl iodide alone, or with the addition of methanol or ethanol, gave solely the methiodide, m. p. 152—153° (from ethanol) (lit.,[5] 155—156°) (Found: C, 43·2; H, 5·0. Calc. for $C_{12}H_{16}IOP$: C, 43·1; H, 4·8%).

Di-(2-ethoxycarbonylethyl)phenylarsine (II; X = As).—Phenylarsine was converted into di-(2-cyanoethyl)phenylarsine (V; X = As), which on hydrolysis gave di-(2-carboxyethyl)-phenylarsine in 86% yield. Hydrogen chloride was passed into a solution of this acid (5 g.) in ethanol (25 c.c.), which was boiled under reflux for 2 hr., cooled, poured into water, and extracted with ether: the washed, dried extract, on distillation, gave the *ester* (II; X = As) (5·5 g., 95%), b. p. 148—150°/0·2 mm., n_D^{22} 1·530 (Found: C, 54·5; H, 6·6. $C_{16}H_{23}AsO_4$ requires C, 54·25; H, 6·5%).

The ester gave a *methiodide*, m. p. 113·5—115°, from ether–ethanol (Found: C, 41·1; H, 5·25. $C_{17}H_{26}AsIO_4$ requires C, 41·1; H, 5·2%). The ester, exposed to moist air, deposited the crystalline spiro-dilactone (VII), m. p. 234—235° (lit.,[8] 235°) (from ethanol) (Found: C, 49·0; H, 4·35. Calc. for $C_{12}H_{13}AsO_4$: C, 48·7; H, 4·4%).

[15] Borsche and Bonaker, *Ber.*, 1921, **54**, 2678.
[16] Grayson, Keough, and Johnson, *J. Amer. Chem. Soc.*, 1959, **81**, 4803.

Ethyl 4-*Oxo*-1-*phenyl*-1-*arsacyclohexane*-3-*carboxylate* (III; X = As).—This entire preparation was carried out under nitrogen. Absolute ethanol (3·2 g.) was added to a stirred suspension of " molecular " sodium (1·6 g., 1 equiv.) in ether (30 c.c.), which was boiled under reflux for 2 hr., then set aside overnight, and the ether was removed. Dry benzene (40 c.c.) and then the ester (II; X = As) (24 g., 1 mol.) were added in turn, and the mixture then boiled under reflux, under a total condensation partial take-off head, so that the benzene–ethanol azeotrope, b. p. 67°, was removed. When the b. p. reached 79°, the mixture was cooled and extracted with water (2 × 100 c.c.). Distillation of the dried benzene layer gave the pure *ester* (III; X = As) (14·8 g., 75%), b. p. 153—154°/1·25 mm., n_D^{26} 1·580 (Found: C, 54·3; H, 5·7. $C_{14}H_{17}AsO_3$ requires C, 54·6; H, 5·5%). It gave a 2,4-*dinitrophenylhydrazone*, yellow needles, m. p. 179—180° (from ethanol) (Found: C, 49·2; H, 4·8; N, 11·75. $C_{20}H_{21}AsN_4O_6$ requires C, 49·2; H, 4·3; N, 11·5%).

5-*Oxo*-1,1′-*diphenyl*-1′-*arsacyclohexano*(4′,3′-3,4)-2-*pyrazoline* (VIII).—A mixture of the ester (0·302 g.), phenylhydrazine (0·120 g.), and acetic acid (1 drop) was heated under nitrogen at 100° for 1 hr. The cold product, when triturated with ether and recrystallised from ethanol, gave the *pyrazoline* (VIII), m. p. 173—174° (Found: C, 61·7; H, 5·5; N, 8·1. $C_{18}H_{17}AsN_2O$ requires C, 61·55; H, 4·8; N, 8·0%. High hydrogen values were obtained despite repeated recrystallisation).

1-*Phenyl*-1-*arsacyclohexan*-4-*one* (IV; X = As).—A mixture of the crude ester (III; X = As) (18·1 g.), concentrated hydrochloric acid (30 c.c.), and ethanol (100 c.c.) under nitrogen was boiled under reflux for 4 hr., cooled, poured into water, and extracted with benzene. Distillation of the extract gave the *oxo-arsine* (IV; X = As) (11·9 g., 89%), b. p. 114—115°/0·3 mm., n_D^{24} 1·612, m. p. 9—10° (Found: C, 55·7; H, 5·7%; *M*, cryoscopic in benzene, 222. $C_{11}H_{13}AsO$ requires C, 55·8; H, 5·5%; *M*, 236). It gave a 4-*phenylsemicarbazone*, m. p. 175—176° (from ethanol) (Found: C, 58·25; H, 5·3; N, 11·5. $C_{18}H_{20}AsN_3O$ requires C, 58·55; H, 5·4; N, 11·4). The low-melting 2,4-dinitrophenylhydrazone could not be purified.

The oxo-arsine (IV; X = As) when boiled with an excess of methyl iodide gave the *methiodide* (IX), m. p. 145—146° after crystallisation from acetone containing a small proportion of ethanol–ether (Found: C, 37·8; H, 4·3; I^-, 34·0. $C_{12}H_{16}AsIO$ requires C, 38·1; H, 4·2; I, 33·6%). Recrystallisation from acetone–ether containing some water gave the 4,4-*dihydroxy*-1-*phenyl*-1-*arsacyclohexane methiodide* (XI), m. p. 120—121° (Found: C, 36·4; H, 4·6; I^-, 32·1 Found, after drying at 60°/0·1 mm. for 36 hr.: C, 36·6; H, 4·5. $C_{12}H_{18}AsIO_2$ requires C, 36·4; H, 4·55; I, 32·1%). The same compound was obtained by the action of methyl iodide on an ethanolic solution of the oxo-arsine.

A solution of the oxo-arsine in an excess of methanolic methyl iodide, when boiled under reflux for 1 hr. and then evaporated, gave 4,4-*dimethoxy*-1-*phenyl*-1-*arsacyclohexane methiodide* (X), having m. p. 146—147° after crystallisation from ethanol or (less wastefully) from ethanol–ether or methanol–ether (Found: C, 39·45; H, 5·5; I^-, 30·55. $C_{14}H_{22}AsIO_2$ requires C, 39·6; H, 5·2; I, 29·95%). The use of carefully dried methanol and methyl iodide in this experiment gave the same product. The methiodide gave a *methopicrate*, yellow needles, m. p. 105·5—108·5° (from water) (Found: C, 45·9; H, 4·7; N, 8·0. $C_{20}H_{24}AsN_3O_9$ requires C, 45·7; H, 4·6; N, 8·0%).

A mixture of the methiodides (IX) and (X) had m. p. 124—125°.

A solution of the methiodide (X) in constant-boiling hydriodic acid (1 vol.) diluted with water (9 vol.), when boiled under reflux for 1 hr. and evaporated, gave a residue, which after repeated crystallisation from ethanol, afforded the methiodide (IX), m. p. and mixed m. p. 144—146°. Conversely, a solution of the methiodide (IX) in methanol with a trace of hydriodic acid, when boiled for 2 hr., gave the crude methiodide (X), m. p. and mixed m. p., 138—139°; the use of ethanol in place of methanol in this experiment gave the crude dihydroxy-methiodide (XI), m. p. 109—110°, identified by its infrared spectrum and by mixed m. p. with the authentic salt (XI).

The Fischer Indolisation.—Interaction of the oxo-phosphine (IV; X = P) (1·1 g.) and phenylhydrazine (0·55 g., 0·89 mol.) in acetic acid (2 c.c.) and water (5 c.c.) gave an oily phenylhydrazone, which was dissolved in ethanol (20 c.c.), to which saturated ethanolic hydrogen chloride (20 c.c.) was then added. The solution was boiled under reflux for 30 min., filtered, cooled, and basified with 10% aqueous sodium hydroxide. The precipitated gum, when recrystallised from ethanol–water (9 : 1 v/v), afforded pale yellow 1,2,3,4-*tetrahydro*-3-*phenyl*-3-*phospha*-9-*azafluorene* (XII) (0·55 g., 37%), m. p. 113—114° (Found: C, 77·0; H, 5·8; N, 5·5.

$C_{17}H_{16}NP$ requires C, 77·0; H, 6·0; N, 5·3%). With hot methyl iodide this gave a brown gum, presumably a dimethiodide, which could not be purified. When heated at 15 mm., this derivative lost methyl iodide, and recrystallisation of the residue from ethanol–ether gave the pale yellow *methiodide*, m. p. 205—206° (Found: C, 52·8; H, 4·95; N, 3·3. $C_{18}H_{19}INP$ requires C, 53·1; H, 4·7; N, 3·4%).

The Friedländer Reaction.—(*A*) 10% Aqueous sodium hydroxide (0·5 c.c.) was added to a solution of the piperidone (IV; X = N) (0·207 g.) and *o*-aminobenzaldehyde (0·148 g., 1·01 mol.) in ethanol (10 c.c.), which was set aside for 96 hr. The solution was then saturated with hydrogen chloride, and the white precipitate collected and added to a mixture of 10% aqueous sodium hydroxide (20 c.c.) and ether (20 c.c.), which was shaken. The dried ethereal layer on evaporation under nitrogen gave an oil, a portion of which was sublimed to give crystals with which the residual oil was seeded. Recrystallisation of the crude base (0·23 g., 75%) from light petroleum (b. p. 60—80°) gave pale yellow 5,6,7,8-*tetrahydro*-6-*phenyl*-2,3-*benzonaphthyridine* (XIII; X = N), m. p. 95—96° (Found: C, 82·95; H, 6·3; N, 10·9. $C_{18}H_{16}N_2$ requires C, 83·1; H, 6·15; N, 10·8%).

An ethanolic solution of this base, when saturated with hydrogen chloride, deposited unstable white crystals for which consistent analyses could not be obtained, but which, on exposure to air, formed the stable yellow *dihydrochloride dihydrate*, needles, m. p. 213·5—215°, from dilute hydrochloric acid (Found: C, 58·4; H, 6·3; N, 7·95; Cl^-, 18·9. $C_{18}H_{16}N_2,2HCl,2H_2O$ requires C, 58·55; H, 6·0; N, 7·6; Cl, 19·2%). This salt, when triturated with a small quantity of water, gave the bright red *monohydrochloride dihydrate*, needles, m. p. 155—156° (from water) (Found: C, 64·85; H, 6·6; N, 8·4; Cl^-, 10·5. $C_{18}H_{16}N_2,HCl,2H_2O$ requires C, 64·95; H, 6·3; N, 8·4; Cl, 10·7%); recrystallisation from hydrochloric acid regenerated the dihydrochloride. The monohydrochloride when heated at 60°/0·1 mm. for 18 hr. afforded the anhydrous *salt*, m. p. 163—164° (E.T.) (Found: C, 72·5; H, 6·2; N, 9·4. $C_{18}H_{16}N_2,HCl$ requires C, 72·8; H, 5·7; N, 9·45%); this was extremely hygroscopic and rapidly reverted in the air to the dihydrate.

Potassium permanganate (in 10% excess) was added to a cold acetone solution of the base (XIII; X = N), which was shaken for 1 hr., filtered, and evaporated. The residual 5-*oxo-derivative* (XV) (yield almost quantitative) recrystallised from light petroleum (b. p. 60—80°) as pale yellow needles, m. p. 152—153° (Found: C, 78·9; H, 5·4; N, 10·1. $C_{18}H_{14}N_2O$ requires C, 78·8; H, 5·1; N, 10·3%).

(*B*) A solution of the oxo-phosphine (IV; X = P) (1 g.) and *o*-aminobenzaldehyde (0·8 g., 1·2 mol.) in ethanol (25 c.c.) containing 10% aqueous sodium hydroxide (0·5 ml.), when set aside for 5 days and then saturated with hydrogen chloride, deposited the colourless *dihydrochloride dihydrate* (1·3 g., 65%) of the base (XIII; X = P), which, after dissolution in ethanol, filtration and reprecipitation with hydrogen chloride, had m. p. 171—172° (Found: C, 56·0; H, 5·8; N, 3·8. $C_{18}H_{16}NP,2HCl,2H_2O$ requires C, 55·8; H, 5·7; N, 3·6%). Basification of an ethanolic solution followed by ether extraction gave 1,2,3,4-*tetrahydro*-2-*phenyl*-10-*aza*-2-*phospha-anthracene* (XIII; X = P), which solidified when seeded with a portion obtained crystalline by distillation, and had m. p. 66·5—67° after recrystallisation from light petroleum (b. p. 40—60°) (Found: C, 78·2; H, 6·0; N, 5·3. $C_{18}H_{16}NP$ requires C, 78·0; H, 5·8; N, 5·3%); it gave a cream-coloured *monomethiodide*, m. p. 212—213° (E.T., T.I., 205°) (from methanol ether) (Found: C, 54·0; H, 4·8; N, 3·4. $C_{19}H_{19}INP$ requires C, 54·4; H, 4·5; N, 3·4%). The dihydrochloride when triturated with water gave the *monohydrochloride dihydrate*, bright yellow needles, m. p. 150—151° (from water) (Found: C, 61·1; H, 6·2; N, 4·2; Cl, 10·45. $C_{18}H_{16}NP,HCl,2H_2O$ requires C, 61·0; H, 5·9; N, 4·0; Cl, 10·2%), which, heated at 60°/0·4 mm. for 24 hr., gave the biscuit-coloured *hydrochloride*, m. p. 178·5—179·5° (E.T.) (Found: C, 68·3; H, 6·0; N, 4·8. $C_{18}H_{16}NP,HCl$ requires C, 68·9; H, 5·4; N, 4·5%); this reverted to the dihydrate slowly on exposure to air and instantly on trituration with water.

(*C*) The preparation of 1,2,3,4-tetrahydro-2-phenyl-10-aza-2-arsa-anthracene (XIII; X = As) proved difficult and unsatisfactory, and was best achieved when the freshly distilled oxo-arsine (IV; X = As) (1·22 g.) and *o*-aminobenzaldehyde (0·97 g.) under nitrogen were heated at 100° for 1 hr. The product, dissolved in ethanol–acetic acid, was partially purified by using Girard's reagent P, and the oily base when then distilled and triturated with light petroleum (b. p. 60—80°) gave a very soluble solid. This material was extracted with cold petroleum, which, when filtered and chilled, deposited crystals, m. p. 76—77°; inconsistent analytical values were obtained on such crystals from different preparations. This base (XIII; X = As)

with dilute hydrochloric acid gave, however, a *hydrochloride hemihydrate*, needles, m. p. 156—157°, from the hot acid (Found: C, 58·5; H, 4·9; N, 3·9. $C_{18}H_{16}AsN,HCl,0{\cdot}5H_2O$ requires C, 58·9; H, 4·6; N, 3·8%); this was unaffected by prolonged heating at 70°/0·1 mm.

The Pfitzinger Reaction.—(*A*) This experiment, including the drying of the analytical specimen, was performed under nitrogen, otherwise an impure product was obtained. A solution of the oxo-amine (IV; X = N) (0·732 g.), isatin (0·663 g., 1·1 mol.), and potassium hydroxide (1·089 g., 4·8 mol.) in ethanol (12 c.c.) and water (3 c.c.) was boiled under reflux for 3 hr., cooled, and poured into 10% aqueous acetic acid (150 c.c.). The precipitated yellow *5,6,7,8-tetrahydro-6-phenyl-2,3-benzonaphthyridine-4-carboxylic acid* (XVI; X = N) (0·45 g., 35%) was insoluble in most solvents, but extraction with boiling ethanol left the pure acid, m. p. 232·5—233·5° (E.T., T.I., 225°) (Found: C, 74·8; H, 5·1; N, 9·4. $C_{19}H_{16}N_2O_2$ requires C, 75·0; H, 5·3; N, 9·2%).

The acid gave a *benzylthiouronium salt*, m. p. 130—133°, which was unaffected by two recrystallisations from ethanol–water (4 : 1, v/v), but changed sharply to 170—171° (decomp.) after two recrystallisations from ethanol–light petroleum (b. p. 60—80°) (4 : 1, v/v). The united mother-liquors from the last two recrystallisations, when concentrated to half-volume, deposited the pure low-melting form, m. p. 134·5—135·5° (decomp.) (Found, for the high- and low-melting form, respectively: C, 68·7, 68·6; H, 5·4, 5·7; N, 11·8, 11·6. $C_{27}H_{26}N_4O_2S$ requires C, 68·9, H, 5·5; N, 11·9%).

(*B*) The oxo-phosphine (IV; X = P) was boiled with alkaline isatin as above for 4·5 hr., cooled, and poured into acetic acid at 0°. The cloudy solution rapidly deposited some tar and then, when set aside at 6°, the pale yellow acid. The total solids were collected and the tarry material removed by hand: the residue (46%) was extracted with boiling ethanol and then sublimed at 210—220°/0·05 mm., giving crystalline *1,2,3,4-tetrahydro-2-phenyl-10-aza-2-phospha-anthracene-9-carboxylic acid* (XVI; X = P), m. p. 248—249° (decomp., E.T., T.I., 225°) (Found: C, 70·95; H, 5·05; N, 4·4. $C_{19}H_{16}NO_2P$ requires C, 71·0; H, 5·0; N, 4·4%). In this preparation, a shorter period of boiling reduces the yield, and a longer period greatly increases the formation of tar.

The acid gave a *benzylthiouronium salt*, m. p. 138·5—139·5°, after crystallisation from ethanol–light petroleum (b. p. 60—80°) (1 : 1 v/v): the mother-liquors, when set aside at 6°, deposited a second form, m. p. 212—214°, raised to 212·5—213·5° by crystallisation from the same solvent (Found, for the high- and low-melting form, respectively: C, 65·3, 63·6; H, 5·3, 5·2; N, 8·4, 8·5. $C_{27}H_{26}N_3O_2PS$ requires C, 66·5; H, 5·3; N, 8·5%. Low carbon values for each form were obtained even after repeated recrystallisations).

(*C*) The use of the oxo-arsine (IV; X = As), with boiling for 4·5 hr. and subsequent extraction with ethanol gave the cream-coloured *acid* (XVI; X = As), m. p. 266—268° (decomp.) (E.T., T.I., 250°) (Found: C, 62·9; H, 4·5; N, 3·9. $C_{19}H_{16}AsNO_2$ requires C, 62·5; H, 4·4; N, 3·8%). It recrystallised from aqueous dimethylformamide and sublimed at 250°/0·05 mm. It gave a stable *benzylthiouronium salt*, m. p. 150—151° [from ethanol–light petroleum (b. p. 60—80°)] (Found: C, 60·9; H, 5·1. $C_{27}H_{26}AsN_3O_2S$ requires C, 61·0; H, 4·9%).

We gratefully acknowledge the gift of a sample of the phosphine (IV; R = P) and preparative directions from Dr. Richard P. Welcher and his co-workers of the American Cyanamid Company, and the award of a University of Queensland Research Scholarship (to M. J. G.).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, May 11th,* 1962.]