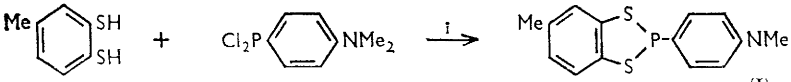
975. *Synthesis and Stereochemistry of Heterocyclic Phosphorus Compounds. Part I. Preparation of* (+)- *and* (−)-10-p-*Dimethylaminophenyl*-9,10-*dihydro*-9-*aza*-10-*phosphaphenanthrene.*

By I. G. M. Campbell and J. K. Way.

The synthesis of a series of 10-aryl-9,10-dihydro-9-aza-10-phosphaphenanthrenes and their oxides is described. The oxide of the 10-*p*-dimethylaminophosphine has been resolved into (+)- and (−)-forms by crystallisation of the camphor-10-sulphonates. Reduction of the (+)- and of the (−)-oxide with lithium aluminium hydride gave the (−)- and the (+)-phosphine respectively. The active phosphines possess considerable optical stability but are too susceptible to atmospheric oxidation to be suitable for racemisation studies. The configuration of the molecule is discussed and the main infrared absorption bands of the compounds are recorded.

Four covalent phosphorus compounds of several different types have recently been isolated in stable optically active forms,[1] but no compounds in which phosphorus occurs in the 3-covalent state have been resolved. Calculations made by Weston [2] on the rate of "racemisation" of trimethylphosphine (*i.e.*, inversion of the pyramidal molecule) indicate a "half-life" of two hours at 7°, so that successful optical resolution of a simple phosphine containing three different groups seems unlikely. However, since enantiomers of tervalent arsenic and antimony compounds in which the metalloid atom is present in a heterocyclic ring have proved unexpectedly stable,[3] we decided to attempt the synthesis and resolution of similar tervalent phosphorus compounds.

The first compound investigated, 2-*p*-dimethylaminophenyl-5-methyl-1,3-dithia-2-phosphaindane (I), was readily obtained in good yield by the route shown. Unfortunately, the pale yellow compound, m. p. 125—126°, failed to form satisfactory salts with tartaric, dibenzoyltartaric, or camphorsulphonic acid, and attempted resolution through a quaternary ammonium salt was precluded because the monomethiodide obtained was unstable and may have been the phosphonium salt, as in the case of 1,4-diphenylhexahydro-1,4-azaphosphorine.[4]



(I)

i, Et_2O–pyridine.

A promising approach to another heterocyclic type was suggested by the relatively simple synthesis of the azaboraphenanthrenes,[5] and Professor Dewar's statement [6] that analogous phosphorus compounds might be obtainable, encouraged us to attempt the synthesis of 10-aryl-9,10-dihydro-9-aza-10-phosphaphenanthrenes (III).

Interaction of phosphorus trichloride with 2-amino- and with 2-amino-4-methylbiphenyl and treatment of the products with aluminium chloride gave cyclic chlorophosphines (II) which were too sensitive to moisture to be readily isolated in a pure state. The crude compounds were therefore arylated directly by means of an aryl-lithium or

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[1] Green and Hudson, *J.*, 1958, 3129, and refs. cited therein; Aaron, Shryne, and Miller, *J. Amer. Chem. Soc.*, 1958, **80**, 107; Aaron, Braun, Shryne, Frack, Smith, Uyeda, and Miller, *ibid.*, 1960, **82**, 596; Kumli, McEwan, and Van der Werf, *ibid.*, 1959, **81**, 248, 3805; Hilgetag and Lehmann, *J. prakt. Chem.*, 1958, **8**, 224; 1959, **9**, 3.

[2] Weston, *J. Amer. Chem. Soc.*, 1954, **76**, 2645.

[3] Campbell and Morrill, *J.*, 1955, 1662; Campbell and Poller, *J.*, 1956, 1195.

[4] Mann and Millar, *J.*, 1952, 3039.

[5] Dewar, Kubba, and Pettit, *J.*, 1958, 3073.

[6] In discussion at the Kekulé Symposium, London, 1958.

Grignard reagent, and the azaphosphaphenanthrenes (III) were obtained in yields ranging from 5 to 25%. The low yields were undoubtedly due, in part, to losses occurring in separating the cyclic chlorophosphines (II) from aluminium chloride by formation of, and filtration from, the $AlCl_3$–$POCl_3$ complex. Purification of the crude products entailed further loss because treatment with charcoal and several crystallisations were required to remove resinous by-products. The properties of the phosphines are listed in Table 1.

TABLE 1. 10-*Aryl*-9,10-*dihydro*-9-*aza*-10-*phosphaphenanthrenes* (III).

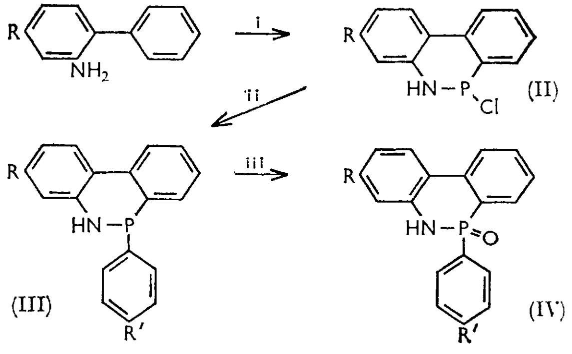
Compound (III)	M. p.	Yield (%)	Found (%) C	H	N	Formula	Required (%) C	H	N
R = R′ = H	181°	11	78·2	5·2		$C_{18}H_{14}NP$	78·55	5·1	5·1
R = Me, R′ = H ...	125—128	25	78·7	5·6	4·95	$C_{19}H_{16}NP$	78·9	5·6	4·8
R = H, R′ = Me ...	135—138	5	78·5	5·7	4·95	$C_{19}H_{16}NP$	78·9	5·6	4·8
R = H, R′ = Br ...	145—147	9	60·9	4·0		$C_{18}H_{13}BrNP$	61·05	3·7	4·0
R = H, R′ = NMe_2	148—153 *	23	75·3	6·2		$C_{20}H_{19}N_2P$	75·5	6·0	8·8

* M. p. 158—160° (sealed tube under nitrogen).

TABLE 2. 10-*Aryl*-9,10-*dihydro*-9-*aza*-10-*phosphaphenanthrene* 10-*oxides* (IV).

Compound (IV)	M. p.	Solvent	Found (%) C	H	N	Formula	Required (%) C	H	N
R = R′ = H	289—290°	EtOH	73·8	4·9	4·6	$C_{18}H_{14}NOP$	74·2	4·8	4·8
R = Me, R′ = H ...	246—248	EtOAc	74·7	5·3	4·75	$C_{19}H_{16}NOP$	74·75	5·3	4·6
R = H, R′ = Me ...	232—235	EtOAc	74·4	5·0	4·75	$C_{19}H_{16}NOP$	74·75	5·3	4·6
R = H, R′ = Br ...	223—226	C_6H_6	58·5	3·7	3·8	$C_{18}H_{13}BrNOP$	58·4	3·5	3·8
R = H, R′ = NMe_2	258—260	EtOAc–EtOH	71·6	5·9	8·5	$C_{20}H_{19}N_2OP$	71·8	5·7	8·4

Like simple aromatic phosphines, the members of the group were stable in air but were readily oxidised by hydrogen peroxide in ethanol at room temperature. Details of the oxides (IV) obtained are given in Table 2. Hydrolysis proved that the heterocyclic ring in the oxide (IV; R = R′ = H) had the structure of an internal amide of a phosphinic acid. The nitrogen–phosphorus bond was stable to hot dilute alkali but was split by boiling with 5N-hydrochloric acid to give the hydrochloride of (2′-amino-2-biphenylyl)phenylphosphinic acid. The ease of ring closure and the stability of the ring system were admirably demonstrated by the fission product which lost water and hydrochloric acid at its melting point, 244°, and re-formed the azaphosphine oxide which melted at 290°.



Reagents: i, PCl_3–$AlCl_3$. ii, ArLi. iii, H_2O_2–EtOH.

Further evidence for the structure of the azaphosphines was obtained from infrared spectra. The main absorption bands of the phosphines and their oxides are listed in Table 3 and are diagnostic of the features of the molecule. The P–Ar, P=O, and P–NH peaks occur at frequencies close to those assigned to them by Bellamy [7] and by Corbridge.[8]

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[7] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1954.

[8] Corbridge, *J. Appl. Chem.*, 1956, **6**, 456.

In the phosphines the P–NH absorption appears as a broad band from 3460 to 3370 cm.$^{-1}$ and in the oxides from 3220 to 3070 cm.$^{-1}$. This shift of 270—300 cm.$^{-1}$ is consistent throughout the series and undoubtedly indicates hydrogen bonding in the oxides. The spectrum of the hydrochloride of (2′-amino-2-biphenylyl)phenylphosphinic acid is included at the end of the Table and shows the characteristic trio of broad shallow bands ascribed to the P(:O)·OH group.[9]

Attempts to resolve the phosphine (III; R = H, R′ = NMe$_2$) were unsuccessful.

TABLE 3. *Main infrared absorption bands of phosphines* (III) *and oxides* (IV) (*cm.*$^{-1}$).

Compounds (III)	
R = R′ = H	3380b, 1600, 1445s, 1430, 1280, 1260, 1160w, 1125w, 900s, 860, 760s, 740s, 725s, 705s
R = Me, R′ = H	3420b, 1615, 1585w, 1425s, 1285, 1240, 1175, 1135, 970, 875, 845, 820, 775s, 745s, 720, 700s, 680
R = H, R′ = Br	3430b, 1605, 1585w, 1430, 1315, 1275, 1235, 1165, 1125, 1070, 1010s, 905s, 810s, 755s, 720s
R = H, R′ = NMe$_2$	3410b, 1595s, 1510, 1445s, 1320, 1275, 1235, 1200w, 1125, 1095s, 1000, 950w, 890s, 860, 810, 775w, 760, 750s, 720
(—)-Form	3410b, 1600s, 1510, 1440s, 1320w, 1275, 1230w, 1200w, 1125, 1095s, 1000w, 950w, 895, 860w, 805, 775, 750s, 720
Compounds (IV)	
R = R′ = H	3110b, 1610, 1595, 1560, 1480, 1440s, 1340, 1285, 1235w, 1200s, 1145, 1125, 1010w, 955s, 870w, 775, 760, 750s, 720s, 690
R = Me, R′ = H	3160b, 1620s, 1595, 1560, 1530, 1435s, 1335w, 1310w, 1290w, 1270w, 1245w, 1200s, 1145, 1120s, 1090s, 1030, 975, 885s, 805, 765s, 750s, 720s, 695s
R = H, R′ = NMe$_2$	3110b, 1600s, 1565w, 1575, 1480s, 1435s, 1365s, 1290, 1270w, 1200s, 1125s, 1085, 1065, 1000, 945s, 870w, 815s, 775s, 755, 720, 690
(—)-Form (R = H, R′ = NMe$_2$) (hydrate)	3400b, 3110bw, 2350b, 1605s, 1565w, 1520, 1480s, 1440s, 1350w, 1285, 1270, 1230, 1165s, 1150s, 1120s, 1085w, 1065w, 1010, 955s, 870w, 805, 780s, 755s, 720, 690
(2′-Amino-2-biphenylyl)phenylphosphinic acid	2640b, 2200b, 2080b, 1595, 1570, 1530, 1500, 1445s, 1315w, 1190, 1165s, 1150s, 1140, 1120, 1100, 950s, 775, 765s, 750, 740, 720, 690s

b = broad band, mid-point; s = strong; w = weak; remainder medium. Nujol peaks: 2950b, 2890b, 1465, 1380.

Salts prepared from a selection of optically active acids separated as gums, and in encouraging these to crystallise it became obvious that this phosphine, in contrast to the other members of the group, was sensitive to atmospheric oxidation when in solution. All the crystalline fractions which were isolated, after periods ranging from three to ten days, proved to be inactive oxide. On the other hand, optical resolution of the oxide (IV; R = H, R′ = NMe$_2$) by crystallisation of the (+)-camphor-10-sulphonate presented no difficulty except that the relative solubilities of the diastereoisomers prevented the isolation of both in optically pure condition. The (—)-oxide formed the less soluble salt with (+)-camphor-10-sulphonic acid and by repeating the resolution with the (—)-acid, salts with $[\alpha]_D$ $-67{\cdot}9°$ and $+67{\cdot}4°$ were obtained.

The active oxides, m. p. 135—136° (decomp. at 145—150°), $[\alpha]_D$ $\pm152°$, regenerated from these salts, crystallised with one molecule of water and were unchanged in melting point and rotation after recrystallisation from ethyl acetate. Hydrated phosphine oxides are not uncommon and their structure is of some interest. Halmann and Pinchas [10] have examined triphenylphosphine oxide hydrate and conclude that the compound is a molecular complex and not the dihydroxide, $Ph_3P(OH)_2$, both from spectral evidence and from lack of ^{18}O exchange. In the active azaphosphine oxides, the water molecule appears to be hydrogen bonded to the P=O group, for the characteristic absorption which appears at 1200 cm.$^{-1}$ in the unhydrated (±)-oxide is shifted to 1165 cm.$^{-1}$ in the hydrates, and the broad P–NH band, found at 3100 cm.$^{-1}$ in the (±)-oxide, is much reduced in the (+)- and the (—)-oxide hydrate, but an absorption band occurs at 3400 cm.$^{-1}$, the position at which

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[9] Braunholtz, Hall, Mann, and Sheppard, *J.*, 1959, 868.

[10] Halmann and Pinchas, *J.*, 1958, 3264.

the phosphine absorbs. This could mean that the usual intermolecular hydrogen bonding in the (±)-oxide cannot occur in the hydrate, but it is also possible that the absorption at 3400 cm.$^{-1}$ is that of the hydrogen-bonded water molecule. A shallow band, not present in the spectra of the oxide, between 2390 and 2310 cm.$^{-1}$ is shown by the hydrate and may indicate a P–OH bond.[9]

Reduction of the (+)-oxide with lithium aluminium hydride in di-n-butyl ether and benzene at 80° [18] gave the phosphine, m. p. 143—148°, with an initial rotation of $[\alpha]_D^{21}$ $-128°$ (in ethyl acetate) which fell to $[\alpha]_D^{21}$ $-97°$ in 4 hr., in the course of which the solution became cloudy and had to be filtered. Thereafter the rotation remained constant. Reduction of the (−)-oxide provided a phosphine, m. p. 154—156°, with $[\alpha]_D^{21}$ $+141°$, which behaved similarly, the initial rotation falling to $[\alpha]_D^{21}$ $+114°$ in 5 hours. That the (−)-phosphine was contaminated with oxide was shown by analysis (carbon, hydrogen, and nitrogen values were slightly low), and by a small P=O peak in the infrared spectrum. Consequently a second specimen of the phosphine was prepared; this had $[\alpha]_D^{21}$ $-138°$ in ethyl acetate and $[\alpha]_D^{19}$ $-221°$ in chloroform. In the latter solvent the initial rotation, α_D^{19} $-1{\cdot}02°$, fell slowly and had reached α_D^{19} $+0{\cdot}20°$ after 18 days at 19—21°. Analysis of the solid regained from this solution indicated it to be mainly oxide. In peroxide-free di-n-butyl ether this phosphine had $[\alpha]_D^{19}$ $-120°$, and when this solution was boiled for 30 min. and cooled a gel was formed. The filtered solution was dextrorotatory and trituration of the gel with ethyl acetate gave oxide which was essentially optically pure ($[\alpha]_D^{20}$ $+150{\cdot}4°$).

Finally, in order to discover whether the fall in rotation in ethyl acetate was the result of racemisation as well as oxidation, a solution, having initially $[\alpha]_D^{20}$ $-138°$ and finally $[\alpha]_D^{20}$ $-112°$ (after 15 hr.), was shaken with hydrogen peroxide and then re-examined polarimetrically. It had $[\alpha]_D^{20}$ $+129{\cdot}5°$, calculated on the basis of complete conversion of the phosphine into hydrated oxide. This is sufficiently close to the rotation of the pure oxide, $[\alpha]_D^{20}$ $+136{\cdot}7°$ in ethyl acetate, to confirm that racemisation of the phosphine had not occurred to any extent. Further, in the course of their preparation the active phosphines withstand heating in boiling benzene for 4—6 hr., so that, in the presence of excess of lithium aluminium hydride, they undoubtedly possess considerable optical stability.

This optical stability is greater than might be expected for a tervalent phosphorus compound if Weston's estimate [2] is valid and, indeed, another possible cause of activity must be considered. Models [11] indicate that in this molecule the nitrogen–phosphorus ring is slightly puckered and the two benzene rings of the biphenyl system are at an angle of approximately 20° to each other. If this system is rigid, the phosphine possesses molecular dissymmetry as well as an asymmetric phosphorus atom and consequently should exist in two racemic modifications. No evidence of this has been obtained. Five different phosphines have been prepared and the product was homogeneous in every case, but the second isomer may have escaped detection in the resinous by-products. However, optical activity has not been observed in " skew " molecules in which the biphenyl system is bridged by two atoms in the 2,2′-positions in the absence of restricting groups in the 6- and 6′-positions. For example, resolution of 9,10-dihydrophenanthrene-2-carboxylic acid has not been achieved [12] although both racemates and three of the four optical isomers of 9-dimethylamino-9,10-dihydro-4,5-dimethylphenanthrene have been isolated.[13] Here, and in the rather similar case of the active 4,6,4′,6′-tetramethylbiphenyl-2,2′-thiolsulphonates,[14] the benzene rings of the biphenyl residue are held in the skew position by the 6,6′-methyl groups. Even biphenyls having a three-carbon-atom bridge and a

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[11] Courtauld models; the phosphorus atom has valency bonds at 109·5° so that the model is not strictly accurate.

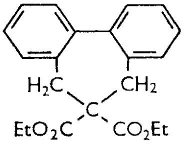
[12] Harris, " Progress in Stereochemistry," Butterworth, London, 1958, Vol. II, p. 181.

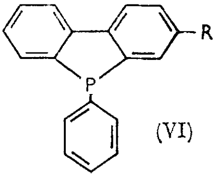
[13] Wittig and Zimmermann, *Chem. Ber.*, 1953, **86**, 629.

[14] Armarego and Turner, *J.*, 1956, 3668.

correspondingly larger angle between the benzene rings resist optical resolution when restricting groups are absent.[15] In fact only one compound without such substituents has been obtained in active form,[16] namely (V), in the (+)-form, and this racemised readily with a half-life of 80 min. at 32·5° in cyclohexane.

(V)





(VI)

Consequently we consider that the stability of the enantiomeric azaphosphaphenanthrenes results from the pyramidal configuration of the phosphorus atom rather than from the skew arrangement of the collinear benzene rings. Proof of this contention is certainly far from complete, but the experimental difficulties arising from the sensitivity of the compound to atmospheric oxidation make it unsuitable for further work. We hope that substituted phosphafluorenes (VI) in which the possibility of a configuration other than pyramidal is unlikely will prove more suitable for stereochemical study.

EXPERIMENTAL

Rotations were measured for absolute EtOH solutions in 2 dm. tubes (*c* 0·25—0·5) at room temperature unless otherwise stated. Infrared measurements were taken for Nujol mulls on the Unicam S.P. 100.

2-p-*Dimethylaminophenyl*-5-*methyl*-1,3-*dithia*-2-*phosphaindane* (I).—Toluene-3,4-dithiol (5 g.) and pyridine (1 ml.) were dissolved together in dry ether (100 ml.), and *p*-dimethylaminophenylphosphonous dichloride[17] (7·2 g.) was added with stirring. Pyridine hydrochloride separated immediately and was rapidly filtered off. The ether solution deposited pale yellow needles, which were recrystallised from ether, giving the *phosphaindane* (I), m. p. 125—126° (4 g., 41%) (Found: C, 59·4; H, 5·5. $C_{15}H_{16}NPS_2$ requires C, 59·1; H, 5·3%).

A mixture of the phosphine (0·5 g.) in dry benzene (25 ml.) and excess of methyl iodide (10 ml.) was kept at 50° for 3 hr. and set aside overnight. The solid which separated recrystallised from ethanol to give a *monomethiodide*, m. p. 125·5—127° (decomp.) (0·2 g.) (Found: C, 42·5; H, 4·3. $C_{16}H_{19}INPS_2$ requires C, 42·9; H, 4·3%). This compound decomposed when kept in a desiccator.

Attempts to prepare analogous compounds by interaction of toluene-3,4-dithiol with phenyl- or with *p*-bromophenyl-phosphonous dichloride under similar conditions failed. In the first case, phenylphosphonic acid, m. p. 158—159°, was the sole product identified. In the second case oxidation did not occur and the product was *p*-bromophenylphosphonous acid, m. p. 143°.

10-*Aryl*-9,10-*dihydro*-9-*aza*-10-*phosphaphenanthrenes* (III) (cf. ref. 5).—2-Aminobiphenyl (8·5 g., 0·05 mole) and phosphorus trichloride (70 ml.) were boiled together with stirring and exclusion of moisture for 8 hr. A precipitate of amine hydrochloride separated almost immediately but redissolved after 5 hr. The dark sticky mass (presumably of $Ar{\cdot}NH{\cdot}PCl_2$) which remained after removal of excess of phosphorus trichloride *in vacuo* was cyclised by heating it at 160—165° with aluminium chloride (0·5 g.) for 6 hr. The product when cold was dissolved in dry benzene, and phosphorus oxychloride (5 ml.) was added. This mixture was boiled under reflux for 0·5 hr. When it cooled, the aluminium chloride–phosphorus oxychloride complex separated and was removed by rapid filtration through glass wool. The clear solution was evaporated to dryness *in vacuo*, giving a pale yellow fuming powder (4·2 g.), m. p. 110—115°. No attempt was made to purify this crude 10-chloro-9,10-dihydro-9-aza-10-phosphaphenanthrene as it was very rapidly hydrolysed by air; it was converted immediately into the required 10-aryl derivative.

9,10-*Dihydro*-10-*phenyl*-9-*aza*-10-*phosphaphenanthrene*.—The crude 10-chloro-compound,

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[15] Turner *et al.*, *J.*, 1952, 854; 1955, 2708; Bell, *J.*, 1952, 1527.

[16] Iffland and Siegel, *J. Amer. Chem. Soc.*, 1958, **80**, 1947.

[17] Michaelis and Schenk, *Ber.*, 1888, **21**, 1497.

[18] Horner, Hoffmann, and Beck, *Chem. Ber.*, 1958, **91**, 1583.

obtained from 0·05 mole of amine, was dissolved in dry benzene (120 ml.), a stream of nitrogen was led in, and phenyl-lithium prepared from bromobenzene (16·2 g.) and lithium (1·5 g.) in ether (100 ml.) was added in 15 min. The mixture was boiled for 1 hr., cooled, and poured into ice-water. The organic layer was separated, dried, and evaporated to 50—60 ml.; colourless needles that separated (2·9 g.) had m. p. 175—178°. Crystallisation (thrice) from benzene gave 9,10-*dihydro*-10-*phenyl*-9-*aza*-10-*phosphaphenanthrene* (1·5 g.), m. p. 180—181° (Found: C, 78·2; H, 5·2. $C_{18}H_{14}NP$ requires C, 78·5; H, 5·1%). Methylation in benzene with methyl iodide at room temperature gave the *methylphosphine methiodide*, m. p. 215·5—216·5° (decomp.) (after crystallisation from ethanol) (Found: C, 55·6; H, 4·4; N, 3·1. $C_{20}H_{19}INP$ requires C, 55·7; H, 4·4; N, 3·25%).

The compounds listed in Table 1 were prepared similarly except that the *p*-bromo-isomer was obtained from the cyclic chloride by interaction with the mono-Grignard reagent from *p*-dibromobenzene. They were crystallised from ethanol or ethanol–ethyl acetate after being boiled with charcoal. Considerable mechanical loss occurred at this stage, but treatment with charcoal proved essential; without it several of the compounds failed to crystallise.

10-*Aryl*-9,10-*dihydro*-9-*aza*-10-*phosphaphenanthrene* 10-*Oxides* (IV).—The oxides were obtained from the pure phosphines, in almost quantitative yield, or from the crude products of the arylation reaction, by addition of hydrogen peroxide (100-vol.) to a solution in ethanol or ethanol–ethyl acetate at room temperature, until a faint turbidity appeared. After being chilled overnight, the oxides were filtered off and recrystallised from the solvents stated in Table **2**.

Hydrolysis of the Phosphine Oxide (IV; R = R′ = H).—The oxide was heated with 5N-hydrochloric acid for 10 hr. and the solid which separated on cooling was recrystallised from 4N-hydrochloric acid, giving (2′-*amino*-2-*biphenylyl*)*phenylphosphinic acid hydrochloride*, m. p. 244° (decomp.) (Found: C, 62·6; H, 4·7; N, 4·2. $C_{18}H_{17}ClNO_2P$ requires C, 62·5; H, 5·0; N, 4·1%). After melting, the compound solidified and remelted at 290°, either alone or mixed with the cyclic oxide.

Attempted Oxidation of 9,10-*Dihydro*-7-*methyl*-9-*aza*-10-*phosphaphenanthrene* 10-*Oxide*.—The oxide (IV; R = Me, R′ = H) (0·45 g.) in pyridine (3 ml.) and water (3·5 ml.) was heated in a water-bath, and potassium permanganate (0·9 g.) was added during 1 hr. The mixture was heated for 3 hr., steam-distilled to remove pyridine, and filtered from manganese dioxide. The filtrate gave no identifiable product and from the manganese dioxide fraction unchanged oxide (0·25 g.) was obtained.

Attempted Optical Resolution of the Phosphine (III; R = H, R′ = NMe_2).—The phosphine (0·4 g.) and (+)-camphor-10-sulphonic acid (0·3 g.) were dissolved together in warm ethanol (5 ml.). No crystalline salt separated and addition of ether precipitated a gum. The solvents were removed *in vacuo* and the residue was dissolved in aqueous ethanol and set aside for several days. The solid which separated (0·16 g.) had m. p. 248—260° and was found to be the oxide (IV; R = H, R′ = NMe_2). Similar results were obtained from using tartaric and dibenzoyltartaric acid.

Optical Resolution of 10-p-*Dimethylaminophenyl*-9-*aza*-10-*phosphaphenanthrene* 10-*Oxide*.—The base (3·3 g.) and (+)-camphor-10-sulphonic acid (2·35 g.) were dissolved together in ethanol (20 ml.) and ethyl acetate (40 ml.) at 75°. The first fraction of salt (3·67 g.), collected after 24 hr., had m. p. 187—195°, $[\alpha]_D$ +11·7°. Evaporation of the mother-liquor to 15 ml. gave a second fraction (1·2 g.) after 24 hr. that had m. p. 210—212°, $[\alpha]_D$ +17·8°, but further evaporation resulted in the separation of free (±)-base, m. p. 253—260° (0·25 g.). No further solid could be obtained from the residues.

The first fraction was extracted with boiling ethyl acetate (2 × 30 ml.), and the residue (2·85 g.) found to have $[\alpha]_D$ 0°. The salt which crystallised from the evaporated extract (0·52 g.) had $[\alpha]_D$ +58·5°. The inactive fraction was crystallised thrice from ethanol–ethyl acetate (1 : 2) to give the (+)-*acid*–(−)-*base salt*, m. p. 203—205°, $[\alpha]_D$ −67·9° (0·45 g.) (Found: C, 63·4; H, 6·5; N, 5·3. $C_{20}H_{19}N_2OP,C_{10}H_{16}O_4S$ requires C, 63·6; H, 6·2; N, 5·0%). Attempts to obtain the more soluble salt in optically pure condition failed, and solutions became brown when kept. The most dextrorotatory fraction obtained (0·52 g.) had $[\alpha]_D$ +58·5° and afforded the oxide with $[\alpha]_D$ +80·7° (0·31 g.). Crystallisation of this from ethyl acetate gave oxide, $[\alpha]_D$ +127·0° (0·16 g.), and a second crystallisation raised the rotation to $[\alpha]_D$ +150·8° ± 1·2° (0·07 g.).

Optically impure (+)-oxide, $[\alpha]_D$ +24·0° (1·6 g.), regained from the resolution, was converted into the (−)-camphor-10-sulphonate, but repeated crystallisation of the first fraction of salt

(2·1 g.), $[\alpha]_D$ +3·6°, failed to yield the optically pure (−)-acid–(+)-base salt. Crystallisation was slow and erratic, apparently because (−)-acid (±)-oxide, $[\alpha]_D$ −17·8°, tended to separate.

To obtain the (+)-isomer, the resolution was repeated with (±)-oxide (3·3 g.) and (−)-camphor-10-sulphonic acid (2·35 g.), dissolved in ethanol (15 ml.) and ethyl acetate (25 ml.). Three fractions of salt were separated; the first, 2·4 g., $[\alpha]_D$ +16·0°, was filtered off after 3 hr.; the second (1·8 g.), $[\alpha]_D$ −39·9°, after evaporation to 15 ml.; and the third, 0·5 g., $[\alpha]_D$ −51·1°, after concentration to 5 ml. and addition of ethyl acetate (5 ml.). Again the last fraction to separate was largely oxide, m. p. 250—260°. Three crystallisations of the first fraction from the minimum volume of ethanol gave (−)-*acid*–(+)-*base salt* (0·37 g.), $[\alpha]_D$ +67·7° (Found: C, 63·7; H, 6·2; N, 4·9%).

Again it proved impossible to isolate the (−)-acid–(−)-base salt in optically pure condition though a fraction (0·13 g.), $[\alpha]_D$ −81·7°, was obtained. The pure salt was prepared by mixing equivalent quantities of the components in ethanol (20 ml.). The specific rotation of this solution was $[\alpha]_D$ −104·3° ± 1·7°. Evaporation of the solvent gave a syrup which crystallised on trituration with ether. The *salt* had m. p. 188—190° (Found: C, 63·3; H, 6·2%).

Isolation of the (+)- *and the* (−)-*oxide*. The (+)-acid–(−)-base salt (0·45 g.) was dissolved in warm ethanol (10 ml.), cooled to −10°, and decomposed with 0·5N-ammonia (15 ml.), and a little water was added. The finely crystalline precipitate was filtered off after 2 hr. at room temperature. The (−)-oxide (0·28 g.) melted at 135—136°, but did not become clear, and at 145—148° became clear and decomposed. It had $[\alpha]_D^{22}$ −152·6° ± 1·2°, and was unchanged in rotation after 4 days at 22° and after being heated in a sealed tube for 3 hr. at 100° (Found: C, 68·2; H, 5·8; N, 7·9. $C_{20}H_{19}N_2OP$ requires C, 71·8; H, 5·7; N, 8·4. $C_{20}H_{19}N_2OP,H_2O$ requires C, 68·2; H, 6·0; N, 7·95%).

The (−)-acid–(+)-base salt (0·58 g.) was decomposed in the same way and gave the (+)-*oxide* (0·34 g.), m. p. 135—136°, decomp. at 144—148°, $[\alpha]_D^{21}$ +152·8° ± 1·2°, unchanged on crystallisation from ethyl acetate (Found: C, 68·4; H, 6·1%).

Reduction of the Optically Active Oxides (cf. ref. 18).—Lithium aluminium hydride (0·15 g.) was suspended in di-n-butyl ether (4·5 ml.) and benzene (10 ml.) at water-bath temperature and the (+)-oxide (0·2 g.) was added in small portions during 45 min. The mixture was heated for 6—7 hr., cooled, and poured into ice-water. The aqueous layer was separated, and the organic layer was filtered and evaporated till only dibutyl ether remained. The product began to crystallise from the ether almost immediately. It was redissolved by addition of hot benzene (5 ml.) and allowed to crystallise. The first fraction of crystals (20 mg.) had m. p. 143—145°.

The solvent was evaporated to 3 ml. and, on chilling, the main product separated (63 mg.), having m. p. 143—148°, $[\alpha]_D^{21}$ −128·0° (*c* 0·2265 in EtOAc) (Found: C, 74·7; H, 5·6; N, 8·5. $C_{20}H_{19}N_2P$ requires C, 75·5; H, 6·0; N, 8·8%). The rotation, α_D^{21} −0·58°, fell to α_D^{21} −0·44° in 4·5 hr., during which the solution became cloudy and was filtered. Thereafter the rotation remained constant for 5 days. Evaporation of the ethyl acetate *in vacuo* left a sticky residue, and solid obtained from this appeared to be oxide (Found: C, 71·4; H, 6·4%).

The reduction was repeated with the (−)-oxide (0·2 g.) under the same conditions, but the period of heating was reduced to 4 hr. after addition of the oxide as a suspension in benzene. Removal of benzene (7 ml.) and chilling gave a first fraction of needles (41 mg.) which proved to be the oxide, $[\alpha]_D^{20}$ −152·4°. When the residual benzene was removed the phosphine (81 mg.) separated from the butyl ether. This specimen had m. p. 154—156°, $[\alpha]_D^{21}$ +141·6° ± 2·3° (*c* 0·219 in EtOAc) (Found: C, 75·7; H, 5·8; N, 8·7%); it behaved in the same way as the (−)-phosphine. The initial rotation, α_D^{21} +0·62°, fell to α_D^{21} +0·50° in 5 hr. and again filtration was necessary.

A second reduction of the (+)-oxide (0·28 g.) gave the (−)-phosphine (0·15 g.), m. p. 153—157°, $[\alpha]_D^{21}$ −138·6° ± 2·2° (*c* 0·225 in EtOAc) (Found: C, 75·3; H, 6·2%). This specimen (46 mg.) was dissolved in chloroform (20 ml.) and had α_D^{20} −1·02°, $[\alpha]_D^{20}$ −221·7°. The rotation dropped slowly at room temperature (19—21°) and after 18 days had reached α_D^{20} +0·20° indicating oxidation. In this case filtration was not necessary (the oxide is very soluble in chloroform). Solid isolated from this solution had C, 69·4; H, 6·3%.

A solution of the phosphine in di-n-butyl ether (freed from peroxides) {$[\alpha]_D^{19}$ −120·6° (*c* 0·228)} was rapidly heated to the b. p., held there for 30 min., and cooled rapidly to 19°. The solution set to a gel. The filtered solution had α_D^{19} +0·10°. The gel was triturated with ethyl acetate, and the crystals obtained (33 mg.) had m. p. 148—156°, $[\alpha]_D^{20}$ + 150·4° ± 2° (*c* 1·138 in EtOH) (Found: C, 68·5; H, 6·2%).

A solution of the phosphine $\{[\alpha]_D^{20}\ -138{\cdot}1°$ (c 0·143 in EtOAc)$\}$ was kept till the rotation had dropped to $[\alpha]_D^{20}\ -112°$. It was then shaken with hydrogen peroxide (100-vol.; 5 ml.) and water (5 ml.) for 10 min. After being dried (Na_2SO_4), the solution had $\alpha_D^{20}\ +0{\cdot}41°$, which represents $[\alpha]_D^{20}\ +129{\cdot}5°$ if conversion into hydrated oxide is complete. {A specimen of the pure (+)-oxide in ethyl acetate (c 0·1755) had $[\alpha]_D\ +136{\cdot}7°$.} Oxide regained from this solution had m. p. 134—138° (decomp. at 150°) (Found: C, 68·0; H, 6·0%).

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