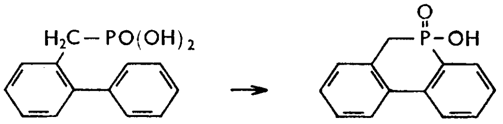
723. 9,10-*Dihydro*-9-*hydroxy*-9-*phosphaphenanthrene* 9-*Oxide, a New Cyclic Phosphinic Acid.*

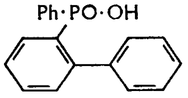
By E. R. Lynch.

Thermal cyclodehydration of 2-phenylbenzylphosphonic acid gives 9,10-dihydro-9-hydroxy-9-phosphaphenanthrene 9-oxide. Derivatives and degradation products of this compound are described. Thermal cyclisation of biphenylylphenylphosphinic acid was also carried out, but 3-phenylpropylphosphonic acid did not cyclise.

The cyclic phosphinic acid (II), 9,10-dihydro-9-hydroxy-9-phosphaphenanthrene 9-oxide, has been obtained by a novel cyclisation of 2-phenylbenzylphosphonic acid. Of the methods so far used for the preparation of cyclic phosphinic acids none was suitable for the present purpose.



(I) (II)



(III)

The diethyl ester of 2-phenylbenzylphosphonic acid (I) was synthesised by an Arbusov reaction between 2-phenylbenzyl chloride and triethyl phosphite. It was hoped to cyclise this acid by the method of Campbell and Way[1] who have cyclised 2-biphenylylphenylphosphinic acid (III) to 9-phenyl-9-phosphafluorene 9-oxide by means of phosphorus pentachloride in nitrobenzene at 180°. This method was unsuccessful in the present case, as also were variations of it involving the use of aluminium chloride. It was found that the chloride derived from the acid (I) could be distilled, or treated with aluminium chloride, without cyclisation. Phosphorus pentachloride, rather than thionyl chloride, was necessary to prepare the acid chloride, for when the acid (I) was treated with thionyl chloride the main product was an anhydride from which the acid (I) was regenerated with water. When this anhydride was strongly heated *in vacuo* there was obtained the required cyclic phosphinic acid (II) along with its anhydride.

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[1] Campbell and Way, *J.*, 1961, 2133.

The above results led to heating the phosphonic acid (I) *in vacuo*, and this gave a mixture of the cyclic phosphinic acid and its anhydride, in proportions varying with the temperature and period of heating. The cyclic acid shows two melting points, one indefinite at 220—225°, the other at 236—238°. Melting at the lower temperature is not always complete in some samples. Besides the elemental analysis, equivalent weight as a monobasic acid, and degradation products, spectroscopic data are not inconsistent with the structure (II). The infrared spectrum (Nujol) of the acid has the trio of bands at $\sim 3{\cdot}7$, 4·3, and 6·0 μ, characteristic of phosphinic acids, compared with bands at 3·6 and 4·3 μ for the parent phosphonic acid (cf. Braunholtz, Hall, Mann, and Sheppard [2]). In the ultraviolet spectra, whereas the parent phosphonic acid shows no *K* band such as is characteristic for biphenyl at 252 mμ, the cyclised acid has a band at 268 mμ ($\varepsilon_{\text{max.}}$ 15,000) which perhaps arises because the two phenyl rings have been twisted towards a coplanar configuration. This absorption recalls that of the analogous arsonium compounds prepared by Cookson and Mann,[3] which exhibit a band at 268—269 mμ. Complete and detailed analysis of the cyclised acid has since been obtained by *X*-ray crystal diffraction,[4] which confirms the structure (II).

Simple derivatives of the cyclic phosphinic acid were prepared: the chloride, anilide, and the methyl and the phenyl ester. The chloride could be obtained from the acid with either phosphorus pentachloride or thionyl chloride, in contrast to the behaviour of 2-phenylbenzylphosphonic acid. Reduction of the chloride with lithium aluminium hydride appears to have given 9,10-dihydro-9-phosphaphenanthrene 9-oxide. Oxidation of the cyclic phosphinic acid with alkaline potassium permangante gave 2′-phosphobiphenyl-2-carboxylic acid, but attempted decarboxylation of this gave no biphenyl-2-phosphonic acid. Instead, there was obtained fluorenone and 9-oxofluorene-4-phosphonic acid, though the latter compound was more readily obtained when the carboxy-phosphonic acid was cyclised in sulphuric acid.

9-Phenyl-9-phosphafluorene 9-oxide was obtained by thermal cyclodehydration of 2-biphenylylphenylphosphinic acid (III) in low yield, but simultaneous pyrolysis also yielded biphenyl and phenylphosphonic acid. When 3-phenylpropylphosphonic acid was heated, water was evolved but only to yield an anhydride of the starting acid, even on prolonged heating *in vacuo* at 350°. Other attempts to cyclise this acid, by several methods, including that of Campbell and Way, also failed.

EXPERIMENTAL

2-Phenylbenzyl Chloride.—2-Phenylbenzyl alcohol (b. p. 173—175°/11 mm.) was prepared in 96% yield by reduction of biphenyl-2-carboxylic acid with lithium aluminium hydride in ether (cf. Goldschmidt and Veer [5]). The alcohol was converted into the chloride (b. p. 104—105°/0·7 mm., n_D^{25} 1·6051; 86% yield) by heating it with an excess of thionyl chloride during 16 hr.

2-Phenylbenzylphosphonic Acid (I).—2-Phenylbenzyl chloride (83 g.) was heated with triethyl phosphite (105 ml.) at 160° during 30 min., then at 200° for a few minutes until evolution of ethyl chloride ceased, with care that triethyl phosphite was not lost by evaporation along with the ethyl chloride. The excess of triethyl phosphite was distilled off at water-pump pressure and the residue was distilled, to yield diethyl 2-phenylbenzylphosphonate (115 g.), b. p. 148—152°/0·3 mm., n_D^{25} 1·5488. The ester was heated under reflux with constant-boiling hydrochloric acid (630 ml.) overnight, to give a clear solution which when cooled gave an oil, rapidly solidifying to crystalline *2-phenylbenzylphosphonic acid* (88 g.), m. p. 167—169° (Found: equiv., 125; C, 62·6; H, 5·1; P, 13·1. $C_{13}H_{13}O_3P$ requires equiv., 124; C, 62·9; H, 5·3; P, 12·5%).

2-Phenylbenzylphosphonic Dichloride and Dianilide.—The phosphonic acid (12·4 g.) was heated with phosphorus pentachloride (21 g.) during 24 hr. on the steam-bath, phosphorus

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[2] Braunholtz, Hall, Mann, and Sheppard, *J.*, 1959, 868.
[3] Cookson and Mann, *J.*, 1949, 2888.
[4] Wheatley, following paper.
[5] Goldschmidt and Veer, *Rec. Trav. chim.*, 1948, **67**, 503.

oxychloride was distilled off, and the residue was distilled, to give the dichloride (9·9 g.), b. p. 150/0·2 mm. No cyclisation had occurred during this operation, for hydrolysis of the product with hot dilute sodium hydroxide solution gave the original phosphonic acid.

The *dianilide*, m. p. 194—195°, was obtained by heating an ethereal solution of the dichloride (2 g.) with aniline (3 g.) during several hours. The white solid was filtered off, washed with water, and recrystallised from ethanol (Found: C, 75·2; H, 5·9; N, 7·0; P, 8·2. $C_{25}H_{23}N_2OP$ requires C, 75·4; H, 5·8; N, 7·0; P, 7·6%).

9,10-*Dihydro*-9-*hydroxy*-9-*phosphaphenanthrene* 9-*Oxide* (II) *and its Anhydride*.—(*a*) *Reaction between* 2-*phenylbenzylphosphonic acid and thionyl chloride*. The phosphonic acid (10 g.) was heated under reflux with thionyl chloride (20 ml.) overnight, the excess of thionyl chloride was distilled off, and the residue heated *in vacuo*, to give a viscous distillate (0·5 g.), b. p. 149—153°/0·2 mm. After being heated for a few minutes longer over a flame *in vacuo* the flask was allowed to cool, and the hard glass was broken up and extracted with ethanol. The ethanolic solution yielded crystals of the cyclic *phosphinic acid*, m. p. 236—238° (also showing a lower indefinite m. p. 220—225°). The titration curve was that of a strong monobasic acid of equivalent weight 228 (calc., 230) (Found: C, 67·4; H, 4·8; P, 13·5. $C_{13}H_{11}O_2P$ requires C, 67·8; H, 4·8; P, 13·5%), $\lambda_{max.}$ (in ethanol) 268 mμ (ε 15,000). That part of the reaction product insoluble in ethanol recrystallised from xylene and then from a large volume of ethanol, to give prisms of the *anhydride* of the cyclic phosphinic acid; this had m. p. 272—276° (Found: C, 70·9; H, 4·6; P, 12·9. $C_{26}H_{20}O_3P_2$ requires C, 70·5; H, 4·6; P, 14·0%). A satisfactory analytical value for phosphorus could not be obtained. Hydrolysis of the anhydride for a few minutes with hot dilute aqueous sodium hydroxide gave a solution which on acidification gave a precipitate of the cyclic phosphonic acid. The distillate (0·5 g.) from the above reaction contained chlorine but it was too impure a sample of the dichloride to give a satisfactory preparation of the dianilide.

In a subsequent reaction between 2-phenylbenzylphosphonic acid (5 g.) and thionyl chloride (10 ml.) the excess of thionyl chloride was distilled off *in vacuo* on the steam-bath. An ethereal solution of the gummy product deposited white solid (3·5 g.), m. p. 204—208°, on storage: this contained no chlorine, and with water it regenerated 2-phenylbenzylphosphonic acid.

(*b*) *Thermal cyclisation of* 2-*phenylbenzylphosphonic acid*. 2-Phenylbenzylphosphonic acid (30 g.) was heated at 350° ± 5° (bath)/0·2 mm. with a nitrogen leak during 6 hr. When cool, the hard glass was broken up and boiled with N-sodium hydroxide (230 ml.) during 10 min. to hydrolyse anhydride. Acidification of the cooled alkaline solution gave a precipitate (25 g.), m. p. *ca*. 210°, which was recrystallised from ethanol, to yield the cyclic phosphinic acid (17·1 g.), m. p. 236—238° (first softening at *ca*. 225° and then hardening again).

When the phosphonic acid (10 g.) was heated at 410° ± 5° (bath)/0·3 mm. during 1 hr., the melt became brown. On cooling, and removal of soluble material by means of ethanol, a residue of the anhydride (3 g.), m. p. 272—274°, was obtained.

Degradation of 9,10-*Dihydro*-9-*hydroxy*-9-*phosphaphenanthrene* 9-*Oxide to Fluorenone and* 9-*Oxofluorene*-4-*phosphonic Acid*.—The cyclic phosphinic acid (1·0 g.), 0·1N-sodium hydroxide (50 ml.), and potassium permanganate were stirred under reflux on the steam-bath during 1 hr. Manganese dioxide was filtered off and the filtrates were acidified with hydrochloric acid and evaporated to dryness. Extraction of the organic material from the residue with moist ether in a Soxhlet apparatus gave 2′-*phosphobiphenyl*-2-*carboxylic acid* (1·0 g.), m. p. 227—230°, which had m. p. 234—237° after recrystallisation from constant-boiling hydrochloric acid (Found: C, 56·5; H, 4·3; P, 10·7. $C_{13}H_{11}O_5P$ requires C, 56·1; H, 4·0; P, 11·1%). This acid is highly soluble in water, with a barium salt soluble in cold but insoluble in hot water.

The carboxy-phosphonic acid (0·5 g.) was heated with copper powder at 260° (bath) during 5 min., then at 300° (bath) during 5 min., and the cooled mixture was partitioned between water and ether. The aqueous phase contained no organic material but gave a yellow precipitate with ammonium molybdate. This result, and the isolation of fluorenone (m. p. 81—82°) from the ethereal phase, indicated that carbon–phosphorus bond scission had occurred rather than decarboxylation. When heated alone at 260° (bath) during 30 min., the carboxy-phosphonic acid again gave fluorenone but also a small quantity of a yellow acid, m. p. 300° (from water). This acid was obtained in high yield by heating the carboxy-phosphonic acid with concentrated sulphuric acid at 110° during 10 min. and adding the red solution obtained to water. Recrystallisation from ethanol gave 9-oxofluorene-4-phosphonic acid, m. p. 306—307·5° (Found: equiv., 131; C, 59·4; H, 3·8; P, 11·0. Calc. for $C_{13}H_9O_4P$: equiv., 130; C, 60·0; H, 3·5; P, 11·9%). Although a satisfactory analysis was not obtained the structure is supported by the ultraviolet spectrum which is similar to that of fluorenone, with peaks at 265 and 256 mμ (ε 52,300 and 40,300 in ethanol) and a broad absorption band of low intensity at 290—330 mμ.

Derivatives of 9,10-*Dihydro*-9-*hydroxy*-9-*phosphaphenanthrene* 9-*Oxide*.—(*a*) Either thionyl chloride or phosphorus pentachloride was used. Thus the acid (12·5 g.) in thionyl chloride (70 ml.) was heated under reflux during 20 hr. and the excess of thionyl chloride was distilled off from the steam-bath, finally *in vacuo*. Remaining traces of thionyl chloride were removed by co-distillation with successive portions of anhydrous benzene until, by removal of the solvent *in vacuo*, a yellow solid was obtained. Recrystallisation from benzene (50 ml.)–light petroleum (55 ml.) gave pale yellow crystals (10·3 g.), m. p. 125—126°, of 9-*chloro*-9,10-*dihydro*-9-*phosphaphenanthrene* 9-*oxide* (Found: Cl, 14·7. $C_{13}H_{10}ClOP$ requires Cl, 14·3%).

(*b*) A solution of the chloride and aniline in benzene was boiled during 90 min., and the white precipitate filtered off, washed with water, and recrystallised from ethanol to give 9-*anilino*-9,10-*dihydro*-9-*phosphaphenanthrene* 9-*oxide*, m. p. 202·5—204° (Found: C, 74·4; H, 5·3; N, 4·5. $C_{19}H_{16}NOP$ requires C, 74·7; H, 5·3; N, 4·6%).

(*c*) A solution of the chloride (2·5 g.), methanol (0·5 ml.), and *NN*-dimethylaniline (1·4 ml.), in benzene (all anhydrous) was boiled under reflux during several hours. Water was added, then the benzene layer was separated and washed with dilute hydrochloric acid. Some acidic material which separated was filtered off, the benzene evaporated, and the residue twice recrystallised from water (the ester also crystallises from light petroleum), to yield 9,10-*dihydro*-9-*methoxy*-9-*phosphaphenanthrene* 9-*oxide*, m. p. 171·5—172·5° (Found: C, 68·7; H, 5·2; P, 12·4. $C_{14}H_{13}O_2P$ requires C, 68·8; H, 5·4; P, 12·7%). The ultraviolet spectrum of the ester in ethanol is essentially the same as that of the parent acid but having a subsidiary peak (ε 8470; $\lambda_{\text{max.}}$ 284 mμ) alongside the major peak (ε 16,000; $\lambda_{\text{max.}}$ 268 mμ).

(*d*) A solution of the chloride [obtained as in (*a*) from the acid (25 g.) but without recrystallisation] in benzene (60 ml.) was added to phenol (10·4 g.) and pyridine (8·8 ml.) in benzene (80 ml.) (all anhydrous). The mixture was heated and stirred under reflux overnight, pyridine hydrochloride was filtered off, and the filtrates were washed with water, dilute sodium hydroxide, and again with water and dried. Distillation yielded 9,10-*dihydro*-9-*phenoxy*-9-*phosphaphenanthrene* 9-*oxide* (15·2 g.), b. p. 197—198°/0·1 mm., m. p. 75—77° (Found: C, 73·8; H, 4·9; P, 10·3. $C_{19}H_{15}O_2P$ requires C, 74·4; H, 4·9; P, 10·1%).

9,10-*Dihydro*-9-*phosphaphenanthrene* 9-*Oxide*.—9-Chloro-9,10-dihydro-9-phosphaphenanthrene 9-oxide (10·3 g.) in anhydrous ether (500 ml.) was added during 2 hr. to lithium aluminium hydride (7 g.) in boiling ether (80 ml.), with stirring under nitrogen. After the mixture had been boiled during a further 4½ hr., water (16 ml.; freed from dissolved oxygen) was carefully added during ½ hr. to the refluxing mixture. The mixture was stirred at the b. p. during 90 min., then cooled, and the heavy precipitate was filtered off and washed with ether, and the combined washings and filtrates were dried ($MgSO_4$). The ether was distilled off under nitrogen and the residue was distilled (negligible residue), to yield three fractions: (i) b. p. 130—135°/0·5 mm.; (ii) b. p. 135—142°/0·5 mm.; (iii) 142—170°/0·5 mm.; all these had a phosphine odour but none was soluble in hydrochloric acid. All the fractions partly crystallised during several weeks under nitrogen. Fraction (ii) was triturated with dioxan and ether, leaving a small crystalline residue, 9,10-*dihydro*-9-*phosphaphenanthrene* 9-*oxide*, m. p. 99—100° (Found: C, 72·7; H, 5·4; P, 14·0. $C_{13}H_{11}OP$ requires C, 72·8; H, 5·2; P, 14·5%). Absorption at 4·29 μ (Nujol) indicates the presence of the P–H group (cf. ref. 6).

2-*Biphenylylphenylphosphinic Acid*.—To a Grignard solution prepared under nitrogen from 2-bromobiphenyl (26·6 g.), magnesium (4·5 g.), and ether (200 ml.) there was added phenylphosphonous dichloride (30 g.) in ether (30 ml.), the heat of reaction keeping the mixture at the b. p. After being stirred at the b. p. during a further 45 min. the mixture was kept overnight, then water (150 ml.) was added dropwise. The solution obtained by combining the ethereal phase with an ethereal extract of the aqueous phase was washed with water and dried (Na_2SO_4). Removal of the ether gave an evil-smelling oil which was taken up in acetone and treated with hydrogen peroxide (20 ml. of 30-vol.), the temperature rising to 45° during the addition. Next day the solution was added to water, the aqueous layer poured off, and the residual oil washed with water. The oil was partitioned between ether and sodium hydroxide

[6] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen and Co. Ltd., London, 2nd edn., 1958, p. 320; Thomas and Chittenden, *Chem. and Ind.*, 1961, 1913.

solution, some insoluble material was filtered off, and the ethereal phase was discarded. Dissolved ether was evaporated from the alkaline solution and the solution was acidified to give a yellowish precipitate (21·5 g.), which, recrystallised from 3 : 1 benzene–light petroleum, gave 2-biphenylylphenylphosphinic acid (13 g.), m. p. 181—182° (lit.,[1] m. p. 180—181°) [anilide, m. p. 204—205° (lit.,[1] m. p. 202—204°)]. This procedure gives a higher yield (39% on 2-bromobiphenyl) than that reported (in ref. 1).

9-*Phenyl*-9-*phosphafluorene* 9-*Oxide*.—2-Biphenylylphenylphosphinic acid (3 g.) was heated at 350° ± 5° (bath)/0·2 mm. during 1 hr. Biphenyl (0·3 g.), m. p. 69—70° (from ethanol), collected in the air condenser. The mixture in the flask was dissolved in benzene and extracted with sodium hydrogen carbonate. Acidification of the alkaline solution gave a precipitate of impure starting material, m. p. 170—173°, which was filtered off, and the filtrates were evaporated to dryness. Extraction of the residue with ethanol gave phenylphosphonic acid (0·45 g.), m. p. 156—159°. The benzene solution was evaporated and the residue was recrystallised from 3 : 1 benzene–light petroleum, to give 9-phenyl-9-phosphafluorene 9-oxide (0·2 g.), m. p. 166—167° (lit.,[1] m. p. 167—168°).

3-*Phenylpropylphosphonic Acid*.—3-Phenylpropyl bromide (79·6 g.) was heated with triethyl phosphite (66·4 g.) at (initially) 160°, rising slowly to 200°; ethyl bromide was allowed to distil off; this yielded diethyl 3-phenylphosphonate (47·4 g.), b. p. 130—139°/0·4 mm. The ester was heated under reflux with constant-boiling hydrochloric acid (300 ml.) during 24 hr., ethyl chloride being allowed to boil off. When cooled, the clear solution gave an oil which crystallised. Recrystallisation from benzene–light petroleum gave 3-*phenylpropylphosphonic acid* (26 g.), m. p. 122—123° (Found: equiv., 101; C, 54·3; H, 6·6; P, 16·4. $C_9H_{13}O_3P$ requires equiv., 100; C, 54·0; H, 6·6; P, 15·4%).

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