

The Thermal Cyclization of Arenylphosphonic Acids. I.
The Synthesis of 4,5-Dihydro-4-hydroxy-4-phosphapyrene-4-oxide (1)

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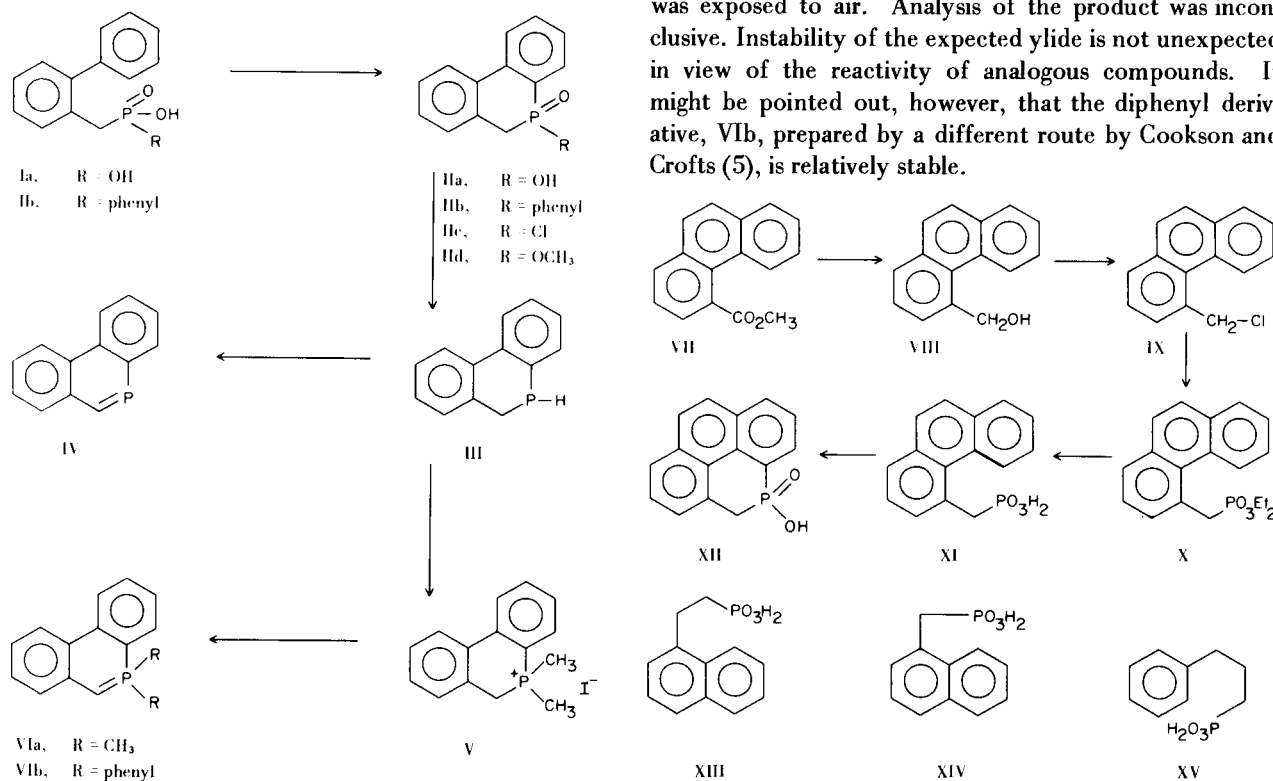
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In 1962, Lynch (3) found that *o*-phenylbenzylphosphonic acid (Ia) and 2-biphenylphenylphosphinic acid (Ib) could be cyclized to derivatives of the 9-phosphaphenanthrene ring system (IIa-b) by heating to 350° *in vacuo*. Although this procedure appears to offer a facile method for the preparation of a number of phosphorus heterocyclic compounds, no further examples of its use have appeared in the literature except for the work of de Koe, *et al.* (4) who repeated the work of Lynch (Ia → IIa) as a means of finally obtaining the unstable 9-phosphaphenanthrene (IV).

Several years ago we began an investigation of this thermal cyclization by repeating and extending Lynch's work toward the preparation of 9,9-dimethyl-9-phosphaphenanthrene (VIa) and toward the preparation of other heterocyclic ring systems. Lynch had attempted to reduce

both the acid, IIa, and the acid chloride, IIc, with lithium aluminum hydride to the phosphine, III, but had been able to isolate only the phosphine oxide. We have found that the methyl ester of this compound (IIId) can be reduced in low yield to the phosphine with lithium aluminum hydride, but that better yields can be obtained by reduction of either the ester or the acid with diphenylsilane. We did not obtain the phosphine in a pure state, but converted the crude reaction product into the *P*-methyl methiodide (V). De Koe (4) has reported the pure phosphine can be obtained in 92 per cent yield by diphenylsilane reduction of the acid.

An attempt was made to prepare the ylide, VIa, by treating the methiodide with phenyllithium under nitrogen. The reaction mixture turned dark and an orange solid separated, but the color quickly faded when this compound was exposed to air. Analysis of the product was inconclusive. Instability of the expected ylide is not unexpected in view of the reactivity of analogous compounds. It might be pointed out, however, that the diphenyl derivative, VIIb, prepared by a different route by Cookson and Crofts (5), is relatively stable.



Attempts have been made to effect the thermal cyclization of three other phosphonic acids, one successfully. Methyl phenanthrene-4-carboxylate (VII) was prepared from naphthalene by the method of Rutherford and Newman (6). This ester was reduced with lithium aluminum hydride, to the alcohol VIII, which was converted *via* the chloride IX, into the phosphonate ester, X. The ester, X, was hydrolyzed to 4-phenanthrylmethylphosphonic acid (XI) which when heated to 355° *in vacuo* cyclized to form 4,5-dihydro-4-hydroxy-4-phosphapyrene-4-oxide (XII), a new heterocyclic ring system.

Two other phosphonic acids were prepared, 1-naphthylmethylphosphonic acid (XIV) and the new 2-(1-naphthyl)ethylphosphonic acid (XIII). Attempts to effect cyclization of these compounds under these conditions, however, were unsuccessful. Lynch (3) also reported that 3-phenyl-1-propylphosphonic acid (XV) did not undergo cyclization by this method. It appears now that, although the reaction is not limited to preparation of the one ring system, it is more limited in scope than was originally envisioned.

EXPERIMENTAL

Melting points were determined using a Mel-Temp capillary melting point apparatus and are uncorrected. Elemental analyses were performed by M-H-W Laboratories, Garden City, Michigan.

9,10-Dihydro-9-methoxy-9-phosphaphenanthrene 9-Oxide (II_d).

In a 500-ml. flask fitted with a condenser and a magnetic stirrer were placed 20 g. (0.087 mole) of 9,10-dihydro-9-hydroxy-9-phosphaphenanthrene 9-oxide (II_a) and 200 ml. of ethyl ether. An ethereal solution of diazomethane was added in 30-ml. portions until the yellow color persisted and stirring was continued for 4 hours after completion of the addition. The flask was placed in the refrigerator overnight, the excess of diazomethane was decomposed with glacial acetic acid, and the white solid was removed by filtration. The product was washed with ether and dried *in vacuo* to give 11.7 g. (55.3%) of the methyl ester, m.p. 168°. The reported m.p. (3) of the ester prepared *via* the acid chloride (II_c) is 171.5-172.5°.

9,10-Dihydro-9-methyl-9-phosphaphenanthrene Methiodide (V).

A mixture of 11.7 g. (0.048 mole) of 9,10-dihydro-9-methoxy-9-phosphaphenanthrene 9-oxide and 13.9 g. (0.075 mole) of diphenylsilane was heated at 190-195° for 4 hours. Distillation gave 2.1 g. of a colorless, oily fraction boiling at 124-136°/1.8 mm. The infrared spectrum of this crude distillate indicated that it was contaminated with unreacted silane so the crude phosphine (III) was treated with 10 ml. of methyl iodide and allowed to stand overnight. The solid which separated was removed by filtration to give 0.5 g. of the methiodide (13.5% from the methyl ester). After being recrystallized 4 times from ethanol, white plates were obtained which melted at 240-242°.

Anal. Calcd. for C₁₅H₁₆PI: C, 50.88; H, 4.52; P, 8.73. Found: C, 50.79; H, 4.32; P, 8.60.

4-Hydroxymethylphenanthrene (VIII).

A solution of 2.2 g. (0.0578 mole) of lithium aluminum hydride in 100 ml. of dry ether was prepared in a 500-ml. flask fitted with

a reflux condenser, a magnetic stirrer, and a dropping funnel. A solution of 13.9 g. (0.0589 mole) of methyl phenanthrene-4-carboxylate (VII) in 100 ml. of dry ether was added dropwise to the flask. When the addition was complete and the vigorous reaction had subsided, the mixture was refluxed for 30 minutes and allowed to stand overnight. After cautious addition of ethanol and water, the metal hydroxides were dissolved in dilute hydrochloric acid. The aqueous and ether layers were separated and the aqueous layer was extracted twice with 100-ml. portions of ether. The combined ether extracts were dried over magnesium sulfate and filtered. After evaporation of the ether, a light yellow solid was obtained which, after recrystallization from ether, gave 10.7 g. (87%) of the alcohol, m.p. 143-144°.

Anal. Calcd. for C₁₅H₁₂O: C, 86.49; H, 5.77. Found: C, 86.30; H, 5.75.

4-Chloromethylphenanthrene (IX).

Seven g. (0.0587 mole) of thionyl chloride was added dropwise to a solution of 10.2 g. (0.0489 mole) of 4-hydroxymethylphenanthrene in 100 ml. of ether. The solution was refluxed until the rapid evolution of hydrogen chloride appeared to cease, the condenser was removed, and the solvent was partially evaporated. After standing overnight the brownish-yellow solid was removed by filtration and recrystallized from ether. A portion of the product was spilled during recrystallization; however, 5 g. (47%) of the chloride, m.p. 68-69°, was recovered.

Anal. Calcd. for C₁₅H₁₁Cl: C, 79.47; H, 4.86; Cl, 15.67. Found: C, 79.34; H, 4.84; Cl, 15.47.

4-Phenanthrylmethylphosphonic Acid (XI).

A solution of 5.0 g. (0.023 mole) of 4-chloromethylphenanthrene (IX) and 8.3 g. (0.0499 mole) of triethyl phosphite in 100 ml. of benzene was refluxed for 5 days. The benzene and unreacted phosphite were then removed under reduced pressure (water aspirator) leaving 5.6 g. (0.0177 mole) of a dark brown oil. Absorption bands at 8.0-8.3μ (P=O), 9.5-9.8μ (p-O-ethyl), and 5.8μ (P-O-ethyl) in the infrared spectrum indicate the presence of the phosphonate ester (X). The crude ester (5.2 g., 0.0158 mole) was hydrolyzed by refluxing for 10 hours with 50 ml. of concentrated hydrochloric acid. The product was placed in the cold overnight, the supernatant liquid was decanted, and oily solid was washed with two 50-ml. portions of ether to give 3.2 g. (57.4% from the chloride) of the phosphonic acid (XI). An analytical sample, recrystallized from ether, melted at 212° with darkening.

Anal. Calcd. for C₁₅H₁₃O₃P: C, 66.42; H, 4.70; P, 11.44. Found: C, 66.24; H, 4.84; P, 11.49.

4,5-Dihydro-4-hydroxy-4-phosphapyrene 4-Oxide (XII).

To a 25-ml. distillation flask was added 1.0 g. (0.0037 mole) of 4-phenanthrylmethylphosphonic acid. The flask was fitted with a nitrogen inlet capillary and evacuated *via* the side arm with a vacuum pump for 15 minutes. The flask was then placed in a Wood's metal bath preheated to 265°. As the material melted, some sublimation of starting acid was noted. After 5.5 hours at the stated temperature evolution of water vapor had apparently ceased. The temperature was increased and maintained in the 250-255° range for an additional 3 hours. The flask was removed from the bath and allowed to cool to room temperature. The vacuum was then broken and an excess of 1N potassium hydroxide was added. This solution was warmed gently until the brown glass-like solid had dissolved and the solution was acidified with concentrated hydrochloric acid to precipitate the acid. This solid was recrystallized from ethanol-water, washed with ether, and finally digested with acetone to remove the brown coloration.

This procedure provided 0.222 g. (0.0087 mole, 22%) of the cyclic product. An analytical sample, recrystallized three times from ethanol, had a m.p. of 255-257°.

Anal. Calcd. for $C_{15}H_{11}O_2P$: C, 70.87; H, 4.33; P, 12.20. Found: C, 70.85; H, 4.51; P, 12.31.

2-(1-Naphthyl)ethyl *p*-Toluenesulfonate.

To a solution of 10 g. (0.058 mole) of 2-(1-naphthyl)ethanol (prepared according to the method of Teuber and Lindner (7)) in 10 ml. of pyridine, cooled to below 0°, was added 12.5 g. (0.064 mole) of *p*-toluenesulfonyl chloride. This mixture was kept below 0° for 2 hours then 100 ml. of water was added, very slowly at first in order to prevent a sudden increase in the temperature. The precipitate that formed was filtered, washed thoroughly with water, and recrystallized from ethanol to give 9.6 g. (50.8%) of the sulfonate, m.p. 58-59°.

Anal. Calcd. for $C_{19}H_{18}SO_3$: C, 69.91; H, 5.55. Found: C, 69.78; H, 5.55.

2-(1-Naphthyl)ethylphosphonic Acid (XIII).

A mixture of 9.0 g. (0.072 mole) of 2-(1-naphthyl)ethyl *p*-toluenesulfonate and 18.2 g. (0.12 mole) of triethyl phosphite was refluxed slowly for 2 days. Vacuum distillation gave 4.0 g. (46.5%) of impure ester, b.p. 180-181°/0.5 mm. This crude ester

was hydrolyzed by refluxing overnight with 15 ml. of concentrated hydrochloric acid. The precipitate that formed on cooling was recrystallized from water to give 0.9 g. (27.6%) of the phosphonic acid, m.p. 166-167°.

Anal. Calcd. for $C_{12}H_{13}PO_3$: C, 61.02; H, 5.50. Found: C, 60.94; H, 5.66.

REFERENCES

- (1) Supported by U.S. Public Health Service Grant No. GM 12480.
- (2) Abstracted from the M.S. theses of William A. Pettit, Thad O. Walker, and Evans R. Shearon and from the research notes of Anil M. Mokashi.
- (3) E. R. Lynch, *J. Chem. Soc.*, 3729 (1962).
- (4) P. de Koe, R. van Veen, and F. Bickelhaupt, *Angew. Chem. Intern. Edit.*, 7, 465 (1968).
- (5) E. A. Cookson and P. C. Crofts, *J. Chem. Soc. (C)*, 2003 (1966).
- (6) K. G. Rutherford and M. S. Newman, *J. Am. Chem. Soc.*, 79, 213 (1957).
- (7) H. -J. Teuber and H. Lindner, *Chem. Ber.*, 92, 926 (1959).