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THE THERMAL CYCLIZATION OF ARENYLPHOSPHONIC ACIDS. II. A NOVEL CYCLODEPHOSPHONATION REACTION

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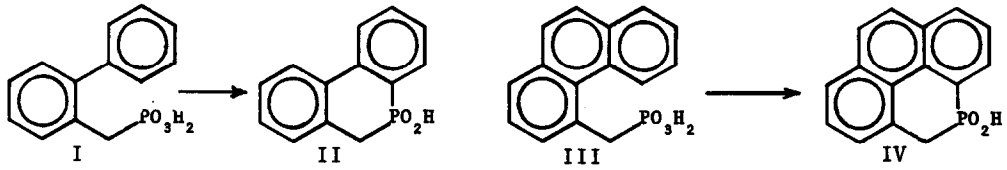
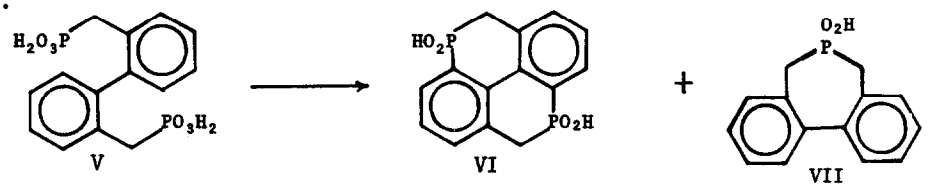
In the first article in this series[2] it was shown that the method used by Lynch[3] for the preparation of 9,10-dihydro-9-hydroxy-9-phosphaphenanthrene 9-oxide (I ⟶ II) could also be used for the preparation of 4,5-dihydro-4-hydroxy-4-phosphapyrene 4-oxide (III ⟶ IV).



I II III IV

In an attempt to extend this reaction toward the preparation of the analogous derivative of the 4,9-diphosphapyrene ring system (VI), 2,2'-di(bromomethyl)biphenyl was prepared according to the method of Underwood and Kochmann[4] and converted into the diphosphonate ester by the Arbusov reaction. The ester was hydrolyzed to the diphosphonic acid (V). The diphosphonic acid was then heated in a sublimation apparatus for 24 hours at 330-370°/1.25 mm to effect cyclization. The combined solid material (sublimate and residue) was dissolved in dilute KOH, decolorized, filtered, and acidified with concentrated hydrochloric acid to give a white solid. This was digested two times for 2 hours each with 75 ml of boiling ethanol and filtered. The residue (10% yield), m.p. 392-395° (dec.), was shown to be the expected product (VI).



V VI VII

The diphosphinic acid itself could not be purified sufficiently for analysis; however, treatment of the acid with an excess of diazomethane converted it into an equimolar mixture of the

cis and trans dimethyl esters of VI: mp 269-272° (from ethyl acetate); uv max ($CHCl_3$) 257 nm (ε=10,900), 266nm (ε=12,800), and 276nm (ε=13,300); ir: 1250 cm^{-1} (P=O) and 1175 and 1030 cm^{-1} (P-O-CH_3); nmr ($CDCl_3$): δ3.3 (4H, d, J=18, -CH_2-), 3.5 (3H, d, J=11, -OCH_3), 3.7 (3H, d, J=11, OCH_3), 7.1-8.1 (6H, ArH); Anal. Found: C, 57.39; H, 4.82; P, 18.37. Calcd for $C_{16}H_{16}O_4P_2$: C, 57.49; H, 4.79; P, 18.56. The two nmr doublets at 3.5 and 3.7δ correspond to the different methoxyl groups in the cis and trans isomers. Lynch[3] has suggested that a uv band at 268nm (ε=15,000) in II might arise because the two phenyl rings have been twisted toward a coplanar configuration by formation of the 6-membered ring; the parent acid (I) and its ester show no such maxima between 250-290nm. It should be noted, however, that in the cyclized acid (II) a new Ar-P=O linkage has been formed which often causes absorption in this area. In either case the assignment of structure VI to our cyclization product is reasonable (the tetraethyl ester of V also shows no such absorption in this area).

The ethanol from the digestion of the cyclization reaction was evaporated to dryness to give a different product (∿30%) to which we have assigned structure VII. This was purified by sublimation at 290°/0.6mm to give a product which melted at 246-248°: Anal. Found: C, 68.89; H, 5.24; P, 13.02. Calcd for $C_{14}H_{13}O_2P$: C, 68.85; H, 5.32; P, 12.71); nmr (CF_3COOD): δ3.2 (4H, d, J=20, -CH_2-), 7.35 (8H, ArH). Diazomethane was also used to convert this compound into its methyl ester: ir: 1240 cm^{-1} (P=O) and 1190 and 1030 cm^{-1} (P-O-CH_3). The uv absorption at 250-290nm is absent in this methyl ester (consistent with either the absence of the Ar-P=O linkage or a less coplanar configuration in the 7-membered ring) and the nmr indicates a ratio of only one -OCH_3 for eight aromatic hydrogens all of which lead to the conclusion that the major product of this cyclization reaction is 6,7-dihydro-6-hydroxy-5H-dibenzo[c,e]phosphepin 6-oxide (VII). The formation of this product suggests that other heterocyclic ring systems might also be prepared by this novel cyclodephosphonation reaction.

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1. Part of the work discussed in this article is abstracted from work presented for the M.S. thesis by William A. Pettit.
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4. H. W. Underwood, Jr., and E. L. Kochmann, J. Amer. Chem. Soc., 46, 2073 (1924).