Tetrahedron Letters No. 38, pp 3365 - 3368, 1976. Pergamon Press. Printed in Great Britain.

A NOVEL CARBON-PHOSPHORUS POLYCATION HETEROCYCLE

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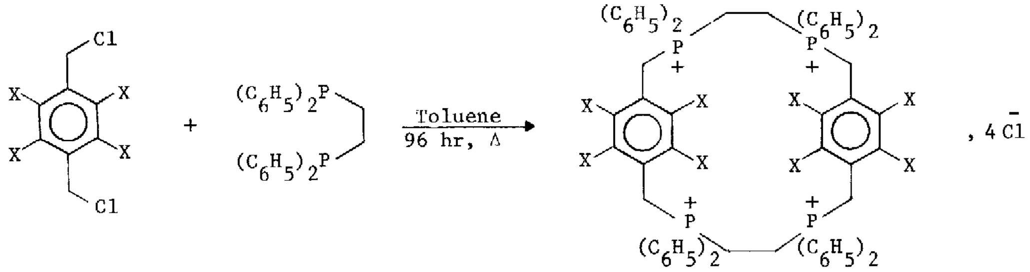
(Received in USA 12 May 1976 ; received in UK for publication 26 July 1976)

Carbon-phosphorus heterocycles with two quaternary phosphorus atoms in a ring have been invariably prepared by reaction of diphosphines with dihalides.[1] A majority of the systems reported by this method, however, fall into 1,4-diphosphoniacyclohexane type.[1] Only a few eight and ten-membered cyclic bisquaternary salts have been recorded in the literature.[2,3] Large-ring phosphorus heterocycles (10 atoms or greater) are rare. Presently, we wish to report the formation of novel macrocycles with four phosphonium groups in a single step in high yield.

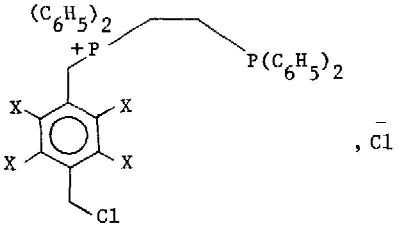
Treatment of 2,3,5,6-tetrachloro-*p*-xylyl dichloride (1a) with ethylenebis(diphenylphosphine) (2) in equal molar ratio in boiling toluene for 4 days (N_2) furnished a single adduct 3a,[4] m.p. 218-220° (from methanol and acetone) in high yield (98%), characterized also as the PF_6^- salt, m.p. 208-210° (from methylene chloride and ether).[4] Likewise, *p*-xylyl dichloride (1b) and diphosphine 2 afforded the adduct 3b, m.p. 328-330° (from large volume of methanol) in good yield (85%). This salt was converted to the corresponding PF_6^- salt, m.p. 310-312° (from methylene chloride and ether),[4] via metathesis of the anion. We propose a cyclic structure 3 for these adducts from the following considerations.



1 2 3

a. X = Cl; b. X = H; c. X = CH_3

Infrared analysis (KBr pellet) of both 3a and 3b showed prominent bands at 1110 and 1430 cm^{-1}, characteristic of P-phenyl phosphonium salts.[3,5] The PMR spectrum (TFA) of 3a exhibited signals centered at δ 3.44 (broad, PCH_2CH_2P), 4.84 (broad, benzylic), 7.68 (multiplet, P-Ar-*H*) and that of 3b at δ 3.16 (broad, PCH_2CH_2P), 4.38 (broad, benzylic), 6.59 (singlet, Ar-*H*) and 7.64 (multiplet, P-Ar-*H*) in the required ratio. Sharp signals in the ^{31}PMR spectra (TFA) of 3a and 3b at -27.26 and -27.41 ppm (relative to 85% H_3PO_4), respectively, established the presence of a phosphonium group. PMR and ^{31}PMR spectral evidence strongly disfavored a simple acylic structure 4 for the adducts. On the basis of spectral analysis as well as a sharp melting point, and solubility in water, a polymeric structure was deemed improbable. Moreover, elemental analysis of the PF_6^- salts could only be satisfactorily accounted for by a cyclic



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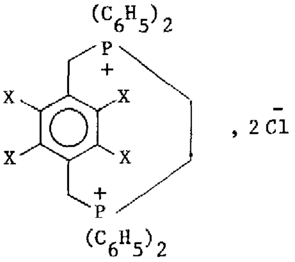
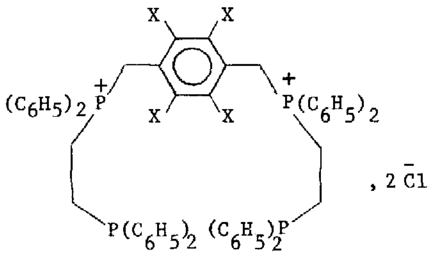


5

structure. However, the alternative cyclic structure 5, although highly unlikely from an examination of courtland models, which suggested that the heterocyclic ring would likely require more than ten atoms to be stable, could not be rejected from considerations. Dimeric structure 3 was finally established *vide infra*.

Interestingly, when the reaction of 1a and 2 was prematurely terminated (3 hr), an acyclic compound 6a, m.p. 240–242° (from isopropanol), was isolated (78%). A PMR spectrum (TFA) of 6a

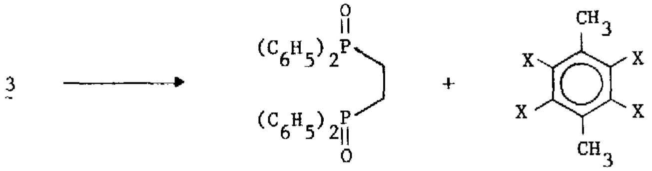


6

a. X = Cl; b. X = H; c. X = CH_3

which had resonance signals centered at δ 3.40 (8 H, m, PCH_2CH_2P), 4.85 (4 H, d, PCH_2, J = 14 Hz, which collapsed to a singlet on ^{31}P decoupling) and 7.45 (40 H, m, P-Ar-H) conclusively established its structure. Two signals at +12.40 and -27.14 ppm (relative to 85% H_3PO_4) were detected in the ^{31}PMR spectrum (methanol) of 6a and supported the presence of a phosphine and a phosphonium group. On changing the solvent to TFA, the signals shifted to -26.12 and -27.16 ppm. This is in agreement with the suspected phosphonium salt and a protonated phosphine. Alternatively, salt 6a was prepared by direct boiling of the dichloride 1a with two equivalents of the diphosphine 2 in benzene (40 hr) in excellent yield (90%). However, all attempts to isolate 6b in the reaction of 1b with 2 failed. Furthermore, the acyclic salt 6b was not formed when the dihalide 1b was boiled in benzene with excess of diphosphine 2. In contrast, salt 6c, m.p. 275–277° (from water)[4] was isolated (35%) in the reaction of 1c with 2 even at the end of a 4-day period along with the major product, the PMR and ^{31}PMR spectral data supported cyclic salt 3c. Additionally, salt 6c was produced by direct boiling of the dihalide 1c with two equivalents of diphosphine 2 in benzene (40 hr) in high yield (93%). Slow addition of 6a to a boiling solution of the dichloride 1a in isopropanol (6 hr) under high dilution followed by further heating (40 hr) afforded the macrocycle or systematically[6] 9,10,19,20,21,22,23,24-octachloro-3,3,6,6,13,13,16,16-octaphenyl-3,6,13,16-tetra-phosphoniatricyclotetracosa-8,10,18,20,21,23-hexaene tetrachloride (3a) (75%). On admixture of this material with the original adduct, the mixed melting point was undepressed. Spectral data of the two compounds also compared in every detail (IR, PMR, ^{31}PMR).

Alkaline hydrolysis of the cyclic salt 3a by boiling with excess of 10% sodium hydroxide (1 hr) furnished a mixture of products from which were isolated ethylenebis(diphenylphosphine)-dioxide (7, 70%) and 2,3,5,6-tetrachloro-*p*-xylene (8a, 80%) as the major products. Likewise, treatment of salt 3b gave the oxide 7 (63%) and *p*-xylene (8b, identified by glc).



7 8

a. X = Cl; b. X = H

There is considerable evidence that alkaline hydrolysis of an acyclic phosphonium salt occurs by apical introduction of hydroxide to form a pentavalent intermediate from which the most electronegative group is expelled as an anion.[7] However, when the phosphorus atom forms a part of a ring, the nature of the products may depend largely on the electronic and steric factors of substituents on phosphorus as well as the strain present in the pentavalent intermediate,[3,7] especially in 5- and 6-membered systems. Fragmentations of the large-ring cyclic salts 3a and 3b closely parallel that of an acyclic phosphonium salt which might imply that the ring is flexible enough to permit preferential loss of the more stable benzylic anion presumably from an apical position.

It may be mentioned that a similar dimeric product containing sulfur as the heteroatom in the ring has been reported in the reaction of *p*-xylyl dibromide with *o*-xylyl dithiol.[8,9,10]

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9. We gratefully acknowledge support of this work by the U.S.P.H.S., National Cancer Institute, CA 11967.
10. The toxicity of polycations **3** and **6** are unknown but have caused swelling of tissue and should be treated with extreme caution. Both compounds have a great propensity to pick up anions and polar organic solvents like $HCCl_3$, alcohols, ethers, etc.