Carbon–Phosphorus Heterocycles. Synthesis of Substituted 1,1′-(α,ω-Alkanediyl)bis(1,2,3,4-tetrahydrophosphinolinium) Salts. A Single-Crystal X-ray Diffraction Analysis of *meso*-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Diperchlorate

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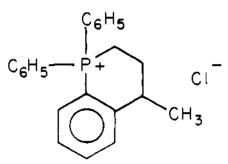
Abstract: Interest in the synthesis of carcinostatic agents which have a central structural element, namely, the 1,2,3,4-tetrahydrophosphinoline ring system, has led to the development of an efficient synthesis of a novel family of 1,1′-(α,ω-alkanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) salts which are dissymmetric because of two asymmetric phosphorus atoms in each of the ring systems. The strategy involved diquaternization of readily available bis(phosphines) followed by cyclization with 115% polyphosphoric acid (PPA) of the resulting open-chain bis(phosphonium) salts to afford the title compounds which always displayed two ^{31}P NMR signals arising from the (±) and meso forms in solution. With 1-chloro-3-methyl-2-butene, bis(diphenylphosphino)methane yielded the phosphinophosphonium salt which formed a mono 1,2,3,4-tetrahydrophosphinolinium salt upon cyclization via 115% PPA. The ^1H NMR, ^{31}P NMR, infrared, and elemental analyses supported the structures of the heterocyclic derivatives. Single-crystal X-ray diffraction analysis of *meso*-1,1′-(1,2-ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) diperchlorate revealed that the molecule assumed a near anti conformation in the solid state with a deviation of C–P dihedral angles from 180 to 143.6° and a slightly flattened ring containing the phosphorus atom. The crystal is monoclinic and the space group is $P2_1/c$. Unit-cell dimensions (at 20 °C) are a = 10.4905 (11) Å, b = 21.694 (3) Å, c = 16.571 (2) Å, β = 105.53 (1)°, and Z = 4. The relative configuration of the substituents at P(1) and P(1)′ are quite different. This X-ray analysis appears to be the initial example for this type of family of C–P heterocycles which have heretofore been unknown. Base-catalyzed hydrolysis of the meso isomer gave the expected phosphine and phosphine oxide which served as an additional proof of structure for the salt.

Carbon–phosphorus (C–P) heterocycles are a class of compounds under very active investigation.[1,2] During the course of studies directed at devising a viable synthetic approach to potential carcinostatic agents which have a central structural element, namely, the 1,2,3,4-tetrahydrophosphinoline ring system, we have had occasion to explore the syntheses and stereochemistry of the title compounds.[3] We report herein the results of that investigation.

Certain carbon–phosphorus heterocycles such as substituted 1,2,3,4-tetrahydrophosphinolinium salts **1** and **2** have displayed



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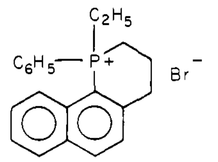

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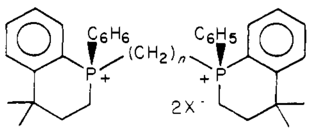
reproducible and good activity against specific cancer systems as demonstrated by the National Cancer Institute during the routine screening process. These are, to the best of our knowledge, rare examples of C–P heterocycles with confirmed carcinostatic activity.[4,5] Moreover, certain α,ω-alkanediylbis(phosphonium) salts have displayed antimicrobial,[6] antihelminitic,[7] and anticholenergic[8] activities. The general formula of the family of targeted compounds is illustrated by **3** (meso form) and by **4** (*dl* pair possible).



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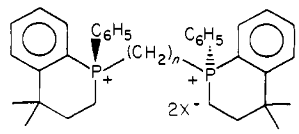

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A search of the literature revealed that no method has existed for the preparation of such bis(tetrahydrophosphinolinium) salts[9] nor has any attempt been made to resolve such systems containing two asymmetric phosphorus atoms in the two rings.[10] This report describes the first synthesis of members of **3** and **4** via a cyclization technique on β-alkenyl-substituted bis(phosphonium) salts.[11] Chemical degradation studies on *meso*-**5a** and single-crystal X-ray diffraction analysis of *meso*-**5b** have provided additional support for the proposed structures of these novel C–P heterocycles.

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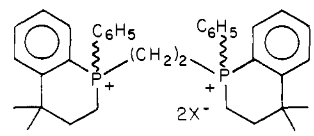


5a, X = Cl
b, X = ClO_4

Separation of **5b** into (±) and meso forms and the resolution of the (±) form into optical antipodes are detailed in the companion paper.[12]

Results and Discussion

Synthesis of 1,1′-(α,ω-Alkanediyl)bis(1,2,3,4-tetrahydrophosphinolinium) Salts. Recent discoveries that β-alkenyl-substituted phosphonium salts,[11a,b] β-alkenyl-substituted phosphine oxides,[11c,13] β-hydroxyalkyl-substituted phosphine oxides,[14] and certain (ω-carboxyalkyl)phosphonium salts[11d] undergo cyclization in polyphosphoric acid (PPA) have provided new entries to C–P heterocycles. Using a similar approach developed in our laboratory,[11] we elected to start from the commercially available bis(phosphines) in an effort to obtain the title compounds. Reaction of 1 equiv of bis(diphenylphosphino)alkane (**6**) with more than 2 equiv of 1-chloro-3-methyl-2-butene at 80 °C in benzene under N_2 afforded the symmetrically substituted, diquaternary phosphonium dichloride **7** which was found to be mildly hygroscopic. For characterization purposes, dichloride **7** was converted to the corresponding bis(hexafluorophosphate) **8** by metathesis using a saturated aqueous solution of KPF_6 at room temperature. However, freshly prepared dichloride **7** underwent cyclization in the presence of 115% PPA[15] at 180 °C for 1 h (Scheme I) to produce 1,1′-(α,ω-alkanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) bis[hexafluorophosphate (1−)] (**9**) via addition of saturated aqueous KPF_6 to the reaction mixture. During cyclization, a gas[11] (presumably HCl) was expelled immediately after the addition of **7** to preheated 115% PPA.

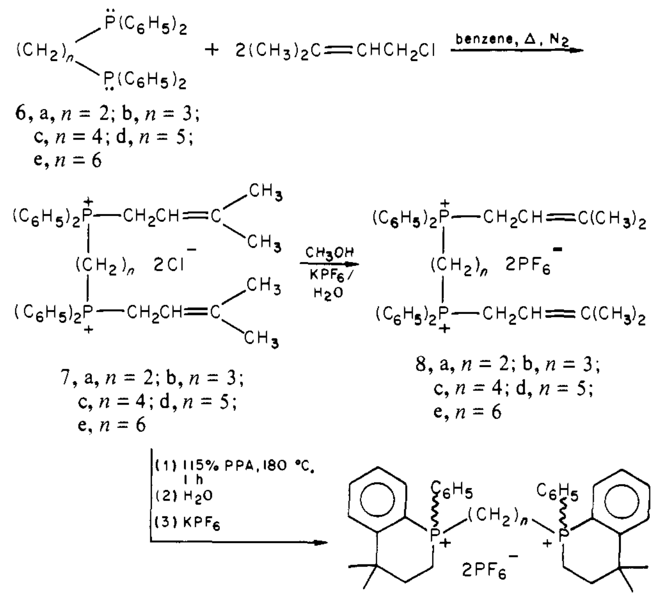
Treatment of bis(diphenylphosphino)methane (**10**) with 1-chloro-3-methyl-2-butene, following the same procedure, gave only the monoalkylated product **11** (converted to and characterized as **12**) (Scheme II). The monochloride **11** did cyclize, however, to **13** in the presence of 115% PPA. Attempts to effect dialkylation of **10** using excess 1-chloro-3-methyl-2-butene at longer reaction periods and at the boiling temperature of different solvents (benzene, toluene, or xylene) gave no indication of formation of dialkylated product as revealed by ^{31}P NMR analysis of the reaction mixture. The reluctance of **10** to form the dialkylated product may possibly be due either to steric hindrance in the starting material to the approaching electrophile or to the decreased basicity of the phosphino moiety of the monoalkylated product **11**. The electron-withdrawing effect of $>P^+<$, which is in close proximity to the phosphino moiety in **11**, reduces the effectiveness of the latter to displace a relatively poor leaving group like Cl^- in an S_N2 reaction. Hussain and Schmidbaur[16] reported only a monoalkylation (even in sealed tube) of **10** with methyl chloride to give **14**, but they were eventually able to prepare the

$$(C_6H_5)_2\ddot{P}{-}CH_2{-}\overset{+}{P}({-}CH_3)(C_6H_5)_2\ Cl^-$$
14

$$[(C_6H_5)_2\overset{+}{P}({-}CH_3){-}CH_2{-}\overset{+}{P}({-}CH_3)(C_6H_5)_2]\ 2Br^-$$
15

dialkylated product **15** using methyl bromide. In our work, dialkylation of **10** to give **16** was finally achieved with 1-bromo-3-methyl-2-butene although the reaction time was long (10 days). Cyclization of the dibromide **16** (converted to and characterized as **17**) with 115% PPA at 205 °C for 1 h gave **18**.

Scheme I



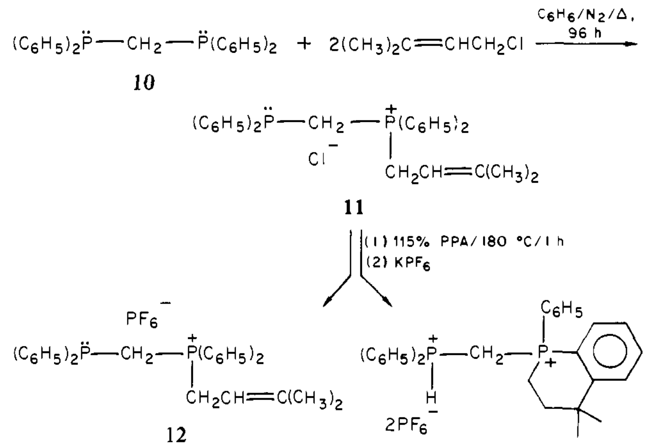
6, a, n = 2; b, n = 3; c, n = 4; d, n = 5; e, n = 6

7, a, n = 2; b, n = 3; c, n = 4; d, n = 5; e, n = 6

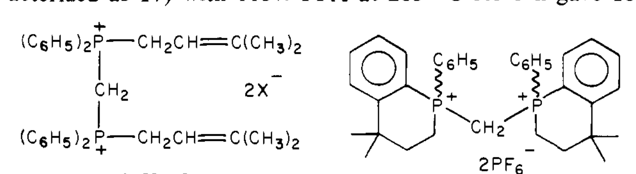
8, a, n = 2; b, n = 3; c, n = 4; d, n = 5; e, n = 6

9a–e

Scheme II



10, 11, 12, 13



16, X = Br
17, X = PF_6

18

With use of our general procedure, diquaternization of bisphosphine **6a** with allyl bromide led to **19** and, with 5-bromo-1-pentene, produced **20** (characterized as **21**). Similarly, diquaternization of **6c** with 4-bromo-1-butene gave **22** (converted to

$$[(C_6H_5)_2\overset{+}{P}({-}R){-}(CH_2)_n{-}\overset{+}{P}({-}R)(C_6H_5)_2]\ 2X^-$$

19, n = 2, R = $-CH_2CH{=}CH_2$, X = Br

20, n = 2, R = $-CH_2CH_2CH_2CH{=}CH_2$, X = Br

21, n = 2, R = $-CH_2CH_2CH_2CH{=}CH_2$, X = PF_6

22, n = 4, R = $-CH_2CH_2CH{=}CH_2$, X = Br

23, n = 4, R = $-CH_2CH_2CH{=}CH_2$, X = PF_6

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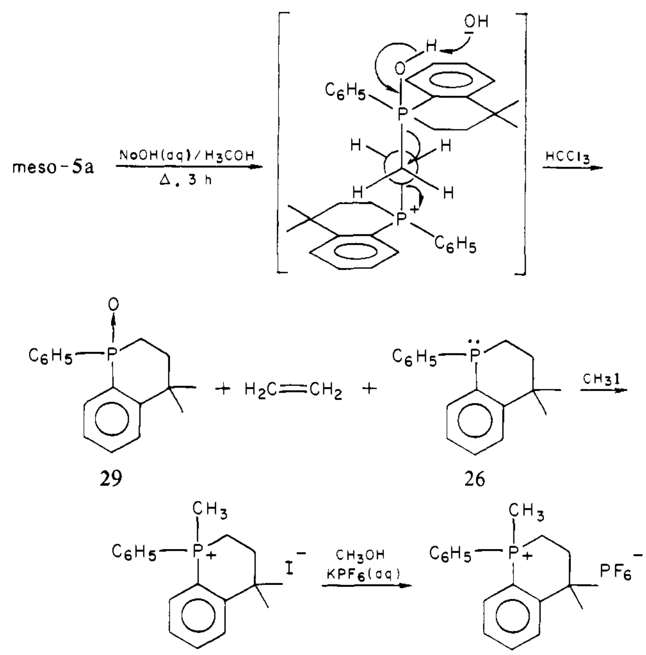
and characterized as **23**). When **21** and **22** were subjected to the general cyclization procedure, several possible isomers formed as revealed by ^{31}P NMR analysis. These isomeric mixtures resisted all attempts at separation and purification. The allyl analogue **19** did *not* cyclize with 115% PPA at 160, 200, 250, and 300 °C as indicated by ^{1}H NMR and ^{31}P NMR analyses of the reaction mixture.

Several workers[5,11b,14] have studied the mechanism of cyclization of β-alkenyl-substituted phosphonium salts in 115% PPA via stereochemical analysis of the products and ^{31}P NMR monitoring of the cyclization process at variable temperatures. The reaction was believed to proceed through a mechanism reminiscent of an acid-catalyzed alkylation of an arene in an electrophilic substitution process. The cyclization of open-chain bis(phosphonium) salts was not limited to chloride or bromide as the anion. Other salts with PF_6 anion could be used. The cyclization of bis(hexafluorophosphate) **8d** to **9d** was achieved by the use of 115% PPA. In early work, a variety of reaction temperatures were tested, and it was found that at temperatures below 160 °C cyclization failed and only a metathesis occurred depending upon the salt added to precipitate the bis(phosphonium) compound from H_2O. At temperatures above 195 °C, extensive charring frequently occurred as was true in reactions noted in this paper.

NMR Analysis of the Title Compounds. Characterization of the 1,1′-(α,ω-alkanediyl)bis(1,2,3,4-tetrahydrophosphinolinium) salts consisted of IR, ^{1}H NMR, ^{31}P NMR, and elemental analyses. All compounds described displayed medium to strong absorption in the regions 1431–1443 and 1110–1120 cm^{-1} in the IR spectra, which have usually been assigned to the C_6H_5–P bond.[17] The absorption in the range 1431–1443 cm^{-1} was considered[18] to be due to a vibration arising from the deformation in the planarity of the phenyl ring bonded to a heavy atom (phosphorus). Compound **13** showed a weak IR band at 2322 cm^{-1} attributable to PH. All β-alkenyl-substituted bis(phosphonium) salts exhibited the doublet of doublets in the ^{1}H NMR spectrum corresponding to the methylene protons adjacent to phosphorus (P—CH_2CH═). These compounds also showed a doublet of doublets for CH_3 protons due to long range $^5J_{P-H}$ coupling. In the ^{31}P-decoupled ^{1}H NMR spectra, the doublet of doublets collapsed to a lone doublet as expected. ^{1}H NMR spectra of the cyclic products were very complex due to severe signal overlap of CH_2 protons in the ring with those of CH_2 protons in the bridge making individual assignments impossible. Although the cyclic products are a mixture of meso and (±) isomers with different conformational preferences, there is no clear rationale at the moment to explain such complex and different signal patterns.

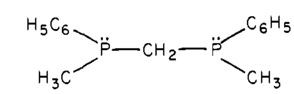
The ^{1}H-decoupled ^{31}P NMR chemical shift values for open-chain bis(phosphonium) salts in our work compare well with those of a few open-chain bis(phosphonium) salts such as 1,3-propanediylbis(triphenylphosphonium) dibromide (+23.2 ppm).[19] Each symmetrically substituted, open-chain bis(phosphonium) salt showed a single peak as expected for identical phosphorus nuclei. An AB spectrum was observed for the unsymmetrical molecule **12** containing two nonidentical P nuclei with $^2J_{PCP}$ = 66.08 Hz. ^{1}H-decoupled ^{31}P NMR spectra of the cyclic bis(phosphonium) salts showed the expected upfield shifts compared to those in open-chain analogues. Benzannelation led to the installation of a double bond adjacent to P(IV) and produced a significant modification in the steric environment about phosphorus. The upfield ^{31}P NMR chemical shifts may be due to the increased electron density at phosphorus as a consequence of dπ–pπ overlap between phosphorus and carbon.[20] The PF_6^- moiety has a value of −143.99, −143.99, −144.12, and −143.92 ppm in **8c**, **9c**, **9e**, and **12**, respectively. The cyclic phosphonium salts always exhibited two ^{31}P NMR signals arising from the meso and racemic-forms

Scheme III



29 26 27 28

in solution. This seems to agree well with the observations that phosphorus atoms in the chiral centers of the meso and racemic forms of **24** and **25** exhibit different ^{31}P chemical shifts.[21] The unsymmetrical salt **13** containing two nonidentical quaternary phosphorus nuclei also showed an AB spectrum with $^2J_{PCP}$ = 10.6 Hz as expected.



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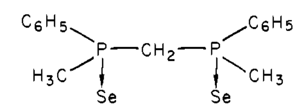

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Chemical Degradation of *meso*-5a. Additional support for the structure identification of bis(tetrahydrophosphinolinium) salts resulted from the base-catalyzed hydrolysis of *meso*-**5a**. Certain 1,2-ethanediylbis(phosphonium) salts have been found to undergo cleavage by alkali into a phosphine and a phosphine oxide with a loss of the two-carbon bridge as ethylene.[22-24] Brophy and Gallagher[23] proposed an E_P mechanism (simultaneous formation of a phosphine oxide, an alkene, and a phosphine) for the alkaline cleavage of 1,2-ethanediylbis(phosphonium) salts based on kinetic studies. Christol and co-workers[24] observed that the base hydrolysis of certain bis(phosphonium) salts at low base concentration occurred by an E_α mechanism, while at high base concentration the hydrolysis proceeded via competing E_P and S_NP (formation of a bis(phosphine) oxide) mechanisms. Following somewhat similar conditions employed by Brophy and Gallagher, related products were isolated from alkaline hydrolysis of *meso*-**5a** (Scheme III). Assuming attack by hydroxide ion on phosphorus, there was a presumable loss of ethylene with concomitant formation of the phosphine **26** which was isolated as the methiodide **27** which in turn was converted to hexafluorophosphate **28**. In addition, phosphine oxide **29** was obtained from the hydrolysis mixture. Properties of both **28** and **29** compared well with those in the literature in all aspects. The anti rotamer of *meso*-**5a** is expected to be heavily populated in solution because of notable steric hindrance and electrostatic repulsion of the like charges of

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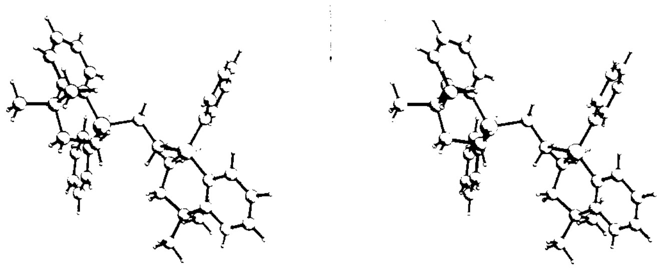

Figure 1. Stereoview of the cation of *meso*-1,1′-(1,2-ethanediyl)bis-(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) diperchlorate (**5b**).

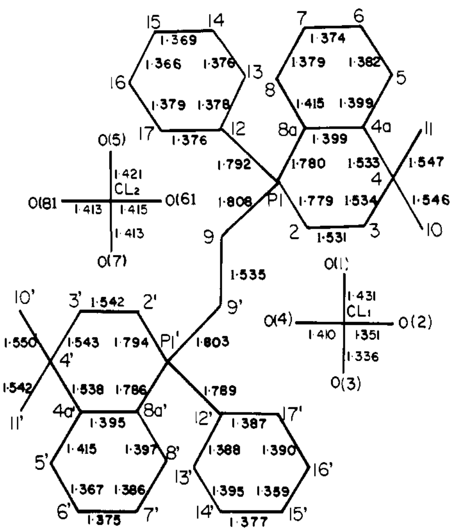

Figure 2. Bond distances and atom numbering. Standard deviations ranges: P–C (0.003–0.004 Å); C–C (0.004–0.007 Å); Cl–O (0.003–0.004 Å) (in *meso*-**5b**).

P groups. We assume a hydroxyphosphorinane intermediate formed which could reasonably contain a pentacovalent phosphorus atom in a trigonal-bipyramid system in which the hydroxy group occupied an apical position. Thus, trans orientation of all groups involved in the subsequent fragmentation and near coplanarity of the P–C–C–P system may favor the synchronous reaction.[25]

Further structural information came from reduction of *meso*-**5a** with lithium aluminum hydride which resulted in the cleavage of *meso*-**5a** to the phosphine **26** with the loss of two-carbon bridge (presumably ethylene).[26] Sodium hydride reduction of *meso*-**5a** also gave similar results, but the yield of phosphine[27] was low. The low yields in these reactions may be reasonable[27] as expected for the sterically crowded phosphonium salt, *meso*-**5a**. Thus identification of chemical degradation products of *meso*-**5a** provides additional support for its structure and was supportive of our general postulated structures for the 1,1′-(α,ω-alkanediyl)-bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) salts. This is further substantiated by the X-ray diffraction data of *meso*-**5b** reported herein.

Single-Crystal Analysis of *meso*-5b. A stereoview of the single molecule of *meso*-**5b** is shown in Figure 1. The bond lengths and atom numbering scheme are shown in Figure 2. The two equivalent halves of the molecule are designated as "unprimed" and "primed" parts. Bond angles are given in Figure 3. Selective torsion angles in the two halves of the molecule are compared in Table I. Figure 4 shows a comparative view of the two equivalent parts of the molecule looking sidewise along the aromatic plane of the phosphinolinium rings.

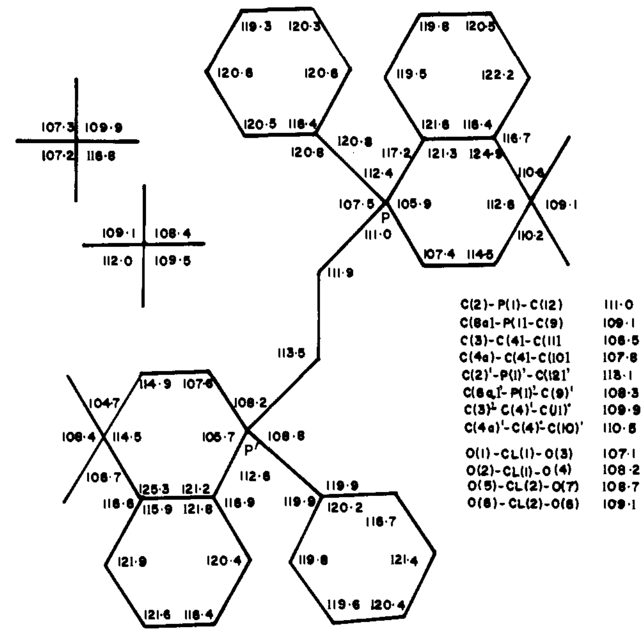

Figure 3. Bond angles. Standard deviations range: 0.2–0.4° (in *meso*-**5b**).

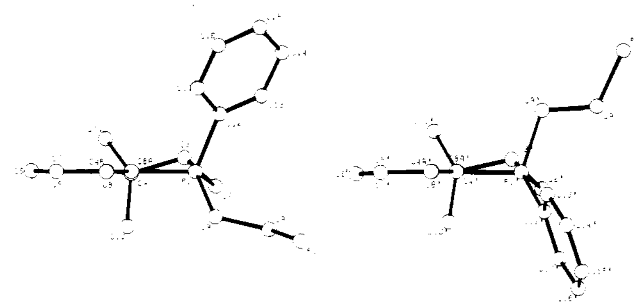

Figure 4. A comparative view of the two equivalent parts of the molecule along the aromatic plane of the phosphinolinium ring in *meso*-**5b**.

Table I. Comparison of Some Selective Torsion Angles in the Two Halves of the Molecule *meso*-5b

	unprimed	primed
C(9)–P(1)–C(2)–C(3)	161.0	−70.9
C(9)–P(1)–C(12)–C(13)	97.3	35.8
C(9)′–C(9)–P(1)–C(2)	46.5	−73.6
C(9)′–C(9)–P(1)–C(8a)	162.8	172.3
C(9)′–C(9)–P(1)–C(12)	−75.1	49.6
P(1)–C(9)–C(9)′–P(1)′	143.6	

In the crystalline state, the potential symmetry of the molecule is destroyed, as is apparent from the torsion angles shown in Table I. The relative configuration of the substituents at P(1) and P(1)′ are quite different. The phenyl group takes an axial position in the unprimed part while it assumes an equatorial position in the primed part (Figure 4).

The heterocyclic ring assumes the familiar half-chair conformation as in other related compounds such as **30**,[5] **31**,[5] **32**,[28] and **2**.[4b] However, there are some significant differences in endocyclic torsion angles between the present structure and those of **30**, **31**, **32**, and **2**. Torsion angles in the heterocyclic ring in these five compounds are compared in Table II, along with the predicted values for a cyclohexene ring.[29] It is expected that the nature

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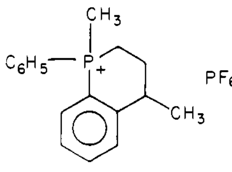

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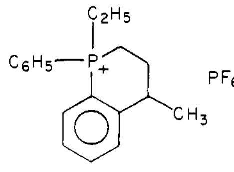

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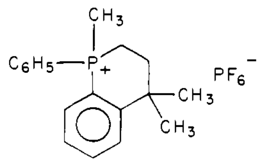

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of the substituents and relative configuration at C(4) and P(1) are the deciding factors in heterocyclic ring conformation. The torsion angles in the present structure differ most from those of compounds **30** and **31** where atom C(4) is partially substituted and compares relatively well with those in compound **32** where C(4) has similar substitution. However, the agreement is even better with those of compound **2** where C(4) is unsubstituted, but the aromatic part is fused with a second ring. The difference in the endocyclic torsion angles in the two parts of the present molecule is quite noticable. This in part may be attributed to a different conformation around the phosphorus atoms. The equatorial phenyl group seems to have brought about a less strained heterocyclic ring in the primed part of the molecule as indicated by a rather surprising agreement of the ring torsion angles in this part with those of a cyclohexene ring (Table II) which were obtained by a strain-minimization procedure.

In general, the bond distances and bond angles in the present structure compare well with those found in a series of phosphorus heterocyclics. The exocyclic P–C distances are somewhat longer than the endocyclic P–C distances. P(1)–C(9) and P(1)′–C(9)′ distances of 1.808 and 1.803 Å are 0.016 and 0.014 Å longer than the P–C(phenyl) distances, P(1)–C(12) [1.792 Å], and P(1)′–C(12)′ [1.789 Å]. This is consistent with the fact that covalent radii of C(sp^3) hybrids are about ~0.03–0.04 Å longer than those of C(sp^2) hybrids. However, in the endocyclic P–C distances, the effects of hybridization are not significant. The P(1)–C(2) [sp^3] and P(1)–C(8a) [sp^2] distances are almost identical, while the corresponding distances in the primed part of the molecule have a difference of only 0.008 Å. These results confirm the observation made earlier[4b,5,28,30] that the phosphorus–carbon distances in phosphorus heterocyclics are affected by a large number of factors including valency, ionization, hybridization, and steric effects and as a result are difficult to correlate with certainty. The C(2)–P(1)–C(8a) endocyclic bond angle in the two phosphorinane rings of the present structure are 105.9 and 105.7°. These values compare well with those observed in compounds **30** (106.6°), **31** (106.6°), **32** (105.7°), and **2** (106.0°). The two phenyl rings are perfectly planar. Root-mean-square deviation of individual atoms from the least-squares planes are 0.008 and 0.002 Å, respectively.

One of the perchlorate groups is slightly disordered. Distances Cl(1)–O(2) of 1.351 Å and Cl(1)–O(3) of 1.336 Å are shorter and the angle O(2)–Cl(1)–O(3) of 116.7° is much larger than the normally expected values.

This X-ray analysis provides unequivocal evidence for the structure of *meso*-**5a** and is supportive of the general postulated structures of the 1,1′-(α,ω-alkanediyl)bis(1,2,3,4-tetrahydrophosphinolinium) salts. A search of literature revealed that no X-ray analysis of this type of compound has been recorded previously.

In this paper, we have described the preparations of the diastereomeric mixtures of 1,1′-(α,ω-alkanediyl)bis(1,2,3,4-tetrahydrophosphinolinium) salts. The separation and resolution of stereoisomers of **5b** have been described elsewhere.[12]

Experimental Section

General Data. Melting points were obtained on a Thomas-Hoover melting point apparatus and were uncorrected. The ^1H and ^{31}P NMR spectra were recorded on a Varian XL-100(15) NMR spectrometer equipped with a Nicolet TT-100 PFT accessory operating at 100.1 MHz for ^1H and at 40.5 MHz for ^{31}P signals with $(CH_3)_4Si$ as internal standard for ^1H and 85% phosphoric acid as external standard for ^{31}P. Infrared spectral data were collected on a Perkin-Elmer 681 spectrophotometer with the samples in potassium bromide pellets. Elemental microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Mass spectral data were collected on a CEC Model 21-110B HR mass spectrometer. Anhydrous solvents such as ether and benzene were dried over sodium and filtered prior to use. Anhydrous THF was obtained by distilling the commercial reagent over sodium hydride first and then from $LiAlH_4$. Unless otherwise specified, commercial reagent grade chemicals were used directly without further purification. Bis(phosphines) were obtained from Strem Chemicals Inc., Danvers, Mass., and were used without further purification. The haloalkenes were distilled immediately before use. The 115% polyphosphoric acid (PPA) was obtained from FMC Corp. Whenever necessary, the experiments were performed under an oxygen-free, dry nitrogen atmosphere.

General Procedure for the Synthesis of Open-Chain Bis(phosphonium) Salts. A typical experiment was performed as follows.

1,2-Ethanediylbis[(3-methyl-2-butenyl)diphenylphosphonium] Bis[hexafluorophosphate(1−)] (8a). A solution of 4.59 g (0.01125 mol) of 1,2-ethanediylbis(diphenylphosphine) (**6a**) in 60 mL of benzene was added dropwise over a period of 3 h from an addition funnel to a preheated solution of 3.14 g (0.03 mol) of 1-chloro-3-methyl-2-butene in 50 mL of benzene in a 250-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, condenser, and N_2 gas inlet. The solution was stirred under reflux for 40 h and allowed to cool to room temperature. Reprecipitation (H_3COH–ether) of the separated solid gave 6.14 g of crude dichloride **7a** which proved exceptionally tedious to purify. This dichloride (1 g) was dissolved in 2 mL of methanol, and the solution was diluted to 4 mL by the addition of water. An addition of an equal volume of saturated aqueous KPF_6 solution resulted in the formation of a heavy precipitate. Reprecipitation (H_2CCl_2–ether) of the solid gave 0.08 g (53% based on bis(phosphine) **6a**) of **8a**: mp 252–254 °C; IR (KBr) ν 1662, 1440, 1120, 997, 845, 730, 690 cm^{-1}; ^1H NMR ($DCCl_3$–TFA, 20:1) δ 1.08 (s, 6 H, CH_3), 1.60 (s, 6 H, CH_3), 2.76–3.26 (m, 4 H, PCH_2CH_2P), 3.32–3.84 (dd, J_{PCH} = 13 Hz, J_{HCCH} = 8 Hz, 4 H, $PCH_2CH{=}C$), 4.64–5.02 (m, 2 H, CH), 7.30–8.04 (m, 20 H, ArH); ^1H-decoupled ^{31}P NMR ($DCCl_3$–TFA, 20:1) +26.48 ppm.

Anal. Calcd for $C_{36}H_{42}P_4F_{12}$: C, 52.31; H, 5.12; P, 14.99. Found: C, 52.18; H, 5.03; P, 15.05.

1,3-Propanediylbis[(3-methyl-2-butenyl)diphenylphosphonium] bis[hexafluorophosphate(1−)] (8b) from 1,3-propanediylbis(diphenylphosphine) (**6b**): 55%; mp 214–215 °C (H_2CCl_2–ether): IR (KBr) ν 1660, 1438, 1122, 997, 844, 735, 688 cm^{-1}; ^1H NMR ($DCCl_3$–TFA, 20:1) δ 1.09 (d, $^5J_{PH}$ = 3.5 Hz, 6 H, CH_3), 1.63 (d, $^5J_{PH}$ = 5.5 Hz, 6 H, CH_3), 1.42–1.92 (m, 2 H, $PCH_2CH_2CH_2P$), 2.70–3.16 (m, 4 H, $PCH_2CH_2CH_2P$), 3.22–3.62 (dd, J_{PCH} = 13 Hz, J_{HCCH} = 8 Hz, 4 H, $PCH_2CH{=}C$), 4.68–5.02 (m, 2 H, CH), 7.32–7.96 (m, 20 H, ArH); ^1H-decoupled ^{31}P NMR ($DCCl_3$–TFA, 20:1) +23.81 ppm (relative to 85% phosphoric acid).

Anal. Calcd for $C_{37}H_{44}P_4F_{12}$: C, 52.87; H, 5.28, P, 14.74. Found: C, 52.94, H, 5.28; P, 14.56.

1,4-Butanediylbis[(3-methyl-2-butenyl)diphenylphosphonium] bis[hexafluorophosphate(1−)] (8c) from 1,4-butanediylbis(diphenylphosphine) (**6c**): 51%; mp 174–175 °C (H_2CCl_2–ether); IR (KBr) ν 1660, 1442, 1118, 1001, 844, 743, 692 cm^{-1}; ^1H NMR ($DCCl_3$–TFA, 20:1) δ 1.16 (d, $^5J_{PH}$ = 3.5 Hz, 6 H, CH_3), 1.63 (d, $^5J_{PH}$ = 5.5 Hz, 6 H, CH_3), 1.44–1.96 (m, 4 H, $PCH_2(CH_2)_2CH_2P$), 2.56–3.04 (m, 4 H, $PCH_2(CH_2)_2CH_2P$), 3.30–3.72 (dd, J_{PCH} = 13 Hz, J_{HCCH} = 8 Hz, 4 H, $PCH_2CH{=}C$), 4.78–5.06 (m, 4 H, CH), 7.32–7.94 (m, 20 H, ArH); ^1H-decoupled ^{31}P NMR ($DCCl_3$–TFA, 20:1) +24.63 ppm.

Anal. Calcd for $C_{38}H_{46}P_4F_{12}$: C, 53.40; H, 5.43; P, 14.50. Found: C, 53.44; H, 5.38; P, 14.65.

1,5-Pentanediylbis[(3-methyl-2-butenyl)diphenylphosphonium] bis[hexafluorophosphate(1−) (8d) from 1,5-pentanediylbis(diphenylphosphine) (**6d**): 78%, mp 232–233 °C (H_2CCl_2–ether); IR (KBr) ν 1660, 1442, 1118, 1001, 844, 743, 690 cm^{-1}; ^1H NMR ($DCCl_3$–TFA, 20:1) δ 1.16 (d, $^5J_{PH}$ = 3.5 Hz, 6 H, CH_3), 1.65 (d, $^5J_{PH}$ = 5.5 Hz, 6 H, CH_3), 1.25–1.80 (m, 6 H, $PCH_2(CH_2)_3CH_2P$), 2.44–2.94 (m, 4 H, $PCH_2(CH_2)_3CH_2P$), 3.26–3.58 (dd, J_{PCH} = 13 Hz, J_{HCCH} = 8 Hz, 4 H, $PCH_2CH{=}C$), 4.76–5.04 (m, 2 H, CH), 7.36–7.94 (m, 20 H, ArH); ^1H-decoupled ^{31}P NMR ($DCCl_3$–TFA, 20:1) +23.76 ppm (relative to 85% phosphoric acid).

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Table II. Comparison of Endocyclic Torsion Angles in *meso*-5b

	30	31	32	2	*meso*-5b unprimed	*meso*-5b primed	cyclohexene analogue
P(1)-C(2)-C(3)-C(4)	−64.2	−60.4	−66.5	−66.0	−67.7	−65.5	62
C(2)-C(3)-C(4)-C(4a)	61.1	59.9	56.7	55.0	56.0	49.8	−45
C(3)-C(4)-C(4a)-C(8a)	−26.3	−31.2	−19.3	−19.0	−20.2	−13.8	15
C(4)-C(4a)-C(8a)-P(1)	−0.4	7.4	−2.1	−2.0	2.4	−0.3	0
C(4a)-C(8a)-P(1)-C(2)	−4.0	−7.9	−7.9	−10.0	−13.7	−15.4	15
C(8a)-P(1)-C(2)-C(3)	33.6	32.9	38.9	43.0	42.8	44.9	−45

Anal. Calcd for $C_{39}H_{48}P_4F_{12}$: C, 53.92, H, 5.57, P, 14.26: Found: C, 54.04; H, 5.71; P, 14.08.

1,6-Hexanediylbis[(3-methyl-2-butenyl)diphenylphosphonium] bis[hexafluorophosphate(1−)] (8e) from 1,6-hexanediylbis(diphenylphosphine) (**6e**): 39%; mp 181–182 °C (H_2CCl_2–ether); IR (KBr) ν 1660, 1442, 1118, 999, 842, 742, 689 cm^{-1}; ^{1}H NMR ($DCCl_3$–TFA, 20:1) δ 1.20 (d, $^5J_{PH}$ = 3.5 Hz, 6 H, CH_3), 1.66 (d, $^5J_{PH}$ = 5.5 Hz, 6 H, CH_3), 1.28–1.58 (m, 8 H, $PCH_2(CH_2)_4CH_2P$), 2.42–2.88 (m, 4 H, $PCH_2(CH_2)_4CH_2P$), 3.24–3.63 (dd, J_{PCH} = 13 Hz, J_{HCCH} = 8 Hz, 4 H, $PCH_2CH{=}C$), 4.76–5.10 (m, 2 H, CH), 7.43–7.90 (m, 20 H, ArH); ^{1}H-decoupled ^{31}P NMR ($DCCl_3$–TFA, 20:1) +24.36 ppm.

Anal. Calcd for $C_{40}H_{50}P_4F_{12}$: C, 54.43; H, 5.71; P, 14.03. Found: C, 54.61; H, 5.76; P, 13.95.

[(Diphenylphosphino)methyl](3-methyl-2-butenyl)diphenylphosphonium hexafluorophosphate(1−) (12) from bis(diphenylphosphino)methane (**10**): 70%; mp 171–172 °C (H_2CCl_2–ether); IR (KBr) ν 1658, 1440, 1115, 999, 844, 742, 689 cm^{-1}; ^{1}H NMR ($DCCl_3$–TFA, 20:1) δ 1.22 (d, $^5J_{PH}$ = 3.5 Hz, 3 H, CH_3), 1.59 (d, $^5J_{PH}$ = 5.5 Hz, 3 H, CH_3), 3.36–3.62 (d, J_{PCH} = 13 Hz, 2 H, PCH_2P), 3.48–3.78 (dd, J_{PCH} = 13 Hz, J_{HCCH} = 8 Hz, 2 H, $PCH_2CH{=}C$), 4.70–5.00 (m, 1 H, CH), 7.20–7.84 (m, 20 H, ArH); ^{1}H-decoupled ^{31}P NMR ($DCCl_3$–TFA, 20:1) +23.80 (d, J_{PCP} = 66.08 Hz, P^+), −30.18 ppm (d, J_{PCP} = 66.08 Hz, $\dot{P}$).

Anal. Calcd for $C_{30}H_{31}P_3F_6$: C, 60.21; H, 5.22; P, 15.53. Found: C, 60.22; H, 5.40; P, 15.62.

Methanediylbis[(3-methyl-2-butenyl)diphenylphosphonium] bis[hexafluorophosphate(1−)] (17) from bis(diphenylphosphino)methane (**10**) and 1-bromo-3-methyl-2-butene (quaternization time, 240 h): 47%; mp 207–209 °C (H_3COH–ether); IR (KBr) ν 1662, 1439, 1114, 998, 844, 744, 685 cm^{-1}; ^{1}H NMR ($DCCl_3$–TFA, 20:1) δ 0.88 (d, $^5J_{PH}$ = 3.5 Hz, 6 H, CH_3), 1.53 (d, $^5J_{PH}$ = 5.5 Hz, 6 H, CH_3), 2.98–3.32 (dd, J_{PCH} = 13 Hz, J_{HCCH} = 8 Hz, 4 H, $PCH_2CH{=}C$), 4.60–5.01 (t, J_{PCH} = 15 Hz, 2 H, PCH_2P, 4.60–5.01 (m, 2 H, CH), 7.48–8.04 (m, 20 H, ArH); ^{1}H-decoupled ^{31}P NMR ($DCCl_3$–TFA, 20:1) +19.97 ppm.

Anal. Calcd for $C_{35}H_{40}P_4F_{12}$: C, 51.74; H, 4.96; P, 15.25. Found: C, 51.65; H, 4.98; P, 14.99.

1,2-Ethanediylbis(allyldiphenylphosphonium) dibromide (19) from 1,2-ethanediylbis(diphenylphosphine) (**6a**) and 3-bromopropene (quaternization time, 24 h), isolated as dibromide: 70%; mp 302–303 °C dec (H_3COH–ether); IR (KBr) ν 1660, 1440, 1118, 998, 738, 691 cm^{-1}; ^{1}H NMR ($DCCl_3$–TFA, 20:1) δ 3.18–3.58 (m, 4 H, PCH_2CH_2P), 4.02–4.44 (dd, J_{PCH} = 13 Hz, J_{HCCH} = 8 Hz, 4 H, $PCH_2CH{=}C$), 5.04–5.60 (m, 6 H, $CH{=}CH_2$) 7.44–8.10 (m, 20 H, ArH); ^{1}H-decoupled ^{31}P NMR ($DCCl_3$–TFA, 20:1) +26.79 ppm.

Anal. Calcd for $C_{32}H_{34}P_2Br_2$: C, 60.02, H, 5.35, P, 9.67. Found: C, 60.22, H, 5.25, P, 9.44.

1,2-Ethanediylbis[(4-pentenyl)diphenylphosphonium] bis[hexafluorophosphate(1−)] (21) from 1,2-ethanediylbis(diphenylphosphine) (**6a**) and 5-bromo-1-pentene (quaternization time, 90 h): 31%; mp 183–185 °C (H_2CCl_2–ether); IR (KBr) ν 1642, 1440, 1118, 998, 844, 741, 689 cm^{-1}; 1.16–1.64 (m, 4 H, $CH_2CH_2CH{=}CH_2$), 1.94–2.28 (m, 4 H, $CH_2CH{=}CH_2$), 2.62–3.08 (m, 8 H, CH_2PCH_2), 4.82–5.79 (m, 6 H, $CH{=}CH_2$), 7.46–8.02 (m, 20 H, ArH); ^{1}H-decoupled ^{31}P NMR ($DCCl_3$–TFA, 20:1) +29.77 ppm.

Anal. Calcd for $C_{36}H_{42}P_4F_{12}$: C, 52.31, H, 5.12, P, 14.99. Found: C, 52.32; J, 5.13; P, 14.75.

1,4-Butanediylbis[(3-butenyl)diphenylphosphonium] bis[hexafluorophosphate(1−)] (23) from 1,4-butanediylbis(diphenylphosphine) (**6c**) and 4-bromo-1-butene (quaternization time, 90 h): 46%; mp 167–168 °C (H_2CCl_2–ether); IR (KBr) ν 1642, 1438, 1118, 997, 844, 743, 688 cm^{-1}; ^{1}H NMR ($DCCl_3$–TFA, 20:1) δ 1.50–1.92 (m, 4 H, $PCH_2(CH_2)_2CH_2P$), 2.02–2.44 (m, 4 H, $CH_2CH{=}CH_2$), 2.58–3.04 (m, 8 H, CH_2PCH_2), 4.92–5.96 (m, 6 H, $CH{=}CH_2$), 7.48–7.93 (m, 20 H, ArH); ^{1}H-decoupled ^{31}P NMR ($DCCl_3$–TFA, 20:1) +26.56 ppm.

Anal. Calcd for $C_{36}H_{42}P_4F_{12}$: C, 52.31, H, 5.12, P, 14.99. Found: C, 52.46; H, 5.24; P, 15.12.

Ring Closure to Produce the 1,1′-(α,ω-Alkanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Salts. The general procedure will be illustrated with the preparation of **9a**.

1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium Bis[hexafluorophosphate(1−)] (9a). The dichloride **7a** (0.91 g, 0.0015 mol) was added over a 10-min period to 40 g of 115% polyphosphoric acid (PPA) which had been heated to 180 °C. The solution was stirred at the same temperature for additional 1-h period, allowed to cool to 110 °C, and poured slowly into 500 g of crushed ice. Upon stirring for 30 min, a homogeneous solution resulted. A saturated KPF_6 solution (50 mL) was added, and the precipitate formed was collected by filtration and dissolved in H_2CCl_2 (10 mL). The aqueous layer was separated, and the organic phase was washed with $NaHCO_3$ solution and H_2O, dried (Na_2SO_4), treated with charcoal, and filtered. The solid was precipitated by the dropwise addition of ether until the solution became cloudy. A second reprecipitation from H_2CCl_2–ether, followed by drying in vacuo, gave 0.50 g (40%) of **9a**: mp 268–270 °C; IR (KBr) ν 1441, 1114, 1000, 844, 741, 688 cm^{-1}; ^{1}H NMR ($DCCl_3$–TFA, 20:1) δ 1.39 (s, 12 H, CH_3), 1.82–3.25 (m, 12 H, CH_2), 7.36–7.96 (m, 18 H, ArH); ^{1}H-decoupled ^{31}P NMR ($DCCl_3$–TFA, 20:1), +15.09, +16.43 ppm.

Anal. Calcd for $C_{36}H_{42}P_4F_{12}$: C, 52.31; H, 5.12; P, 14.99. Found: C, 52.19; H, 5.30; P, 14.82.

1,1-(1,3-Propanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) bis[hexafluorophosphate(1−)] (9b) from the dichloride **7b**: 51%; mp 243–245 °C (H_2CCl_2–ether); IR (KBr) ν 1440, 1116, 998, 844, 739, 690 cm^{-1}; ^{1}H NMR ($DCCl_3$–TFA, 20:1) δ 1.14–1.48 (m, 12 H, CH_3), 1.66–3.38 (m, 14 H, CH_2), 7.34–7.98 (m, 18 H, ArH); ^{1}H-decoupled ^{31}P NMR ($DCCl_3$–TFA, 20:1) +12.50, +12.92 ppm.

Anal. Calcd for $C_{37}H_{44}P_4F_{12}$: C, 52.87; H, 5.28; P, 14.74. Found: 52.69; H, 5.35; P, 14.69.

1,1′-(1,4-Butanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) bis[hexafluorophosphate(1−)] (9c) from the dichloride **7c**: 45%; mp 214–215 °C (H_2CCl_2–ether); IR (KBr) ν 1440, 1118, 998, 844, 741, 690 cm^{-1}; ^{1}H NMR ($DCCl_3$–TFA, 20:1) δ 1.40 (s, 12 H, CH_3), 1.50–3.20 (m, 16 H, CH_2), 7.28–7.92 (m, 18 H, ArH); ^{1}H-decoupled ^{31}P NMR ($DCCl_3$–TFA, 20:1) +13.28, +13.37 ppm.

Anal. Calcd for $C_{38}H_{46}P_4F_{12}$: C, 53.40, H, 5.43, P, 14.50. Found: C, 53.15; H, 5.35; P, 14.26.

1,1′-(1,5-Pentanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) bis[hexafluorophosphate(1−)] (9d) from the bis(hexafluorophosphate) **8d**: 30%; mp 148–150 °C (H_2CCl_2–ether); IR (KBr) ν 1442, 1119, 1001, 844, 752, 691 cm^{-1}; ^{1}H NMR ($DCCl_3$–TFA, 20:1) δ 1.40 (s, 12 H, CH_3), 1.14–3.84 (m, 18 H, CH_2), 7.32–7.98 (m, 18 H, ArH); ^{1}H-decoupled ^{31}P NMR ($DCCl_3$–TFA, 20:1) +13.02, +13.08 ppm.

Anal. Calcd for $C_{39}H_{48}P_4F_{12}$: C, 53.92; H, 5.57; P, 14.26. Found: C, 54.06; H, 5.76; P, 14.40.

1,1′-(1,6-Hexanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) bis[hexafluorophosphate(1−)] (9e) from the dichloride **7e**: 31%; mp 113–117 °C (H_2CCl_2–ether); IR (KBr) ν 1442, 1119, 1000, 844, 752, 692 cm^{-1}; ^{1}H NMR ($DCCl_3$–TFA, 20:1) δ 1.43 (s, 12 H, CH_3), 1.14–3.08 (m, 20 H, CH_2), 7.38–8.06 (m, 18 H, ArH); ^{1}H-decoupled ^{31}P NMR ($DCCl_3$–TFA, 20:1), +13.91, +13.96 ppm.

Anal. Calcd for $C_{40}H_{50}P_4F_{12}$: C, 54.43; H, 5.71; P, 14.03. Found: C, 54.52; H, 5.84; P, 14.07.

1-[(Diphenylphosphonio)methyl]-1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium Bis[hexafluorophosphate(1−)] (13). The chloride **11** (2.0 g, 0.004 mol) underwent cyclization when treated with 50 g of 115% polyphosphoric acid at 175 °C for 1 h. The solution was cooled to 120 °C and was slowly poured into 500 mL of ice-water. This resulted in the formation of a homogeneous solution after stirring for 15 min. Upon the addition of 50 mL of saturated aqueous KPF_6 solution, precipitation of the crude solid occurred. The crude solid was filtered and dissolved in H_3CCN (ca. 45 mL). A small aqueous layer separated and the organic phase was drawn off and dried (Na_2SO_4). Reprecipitation of the solid was effected from the H_3CCN solution by the dropwise addition of ether until the solution became cloudy. A second reprecipitation (H_3CCN–ether) gave 1.55 g (52%) of **13**: mp 290–292 °C; IR (KBr) ν 2322, 1438, 1110, 999, 844, 740, 688 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 1.58 (s, 3 H, CH_3), 1.78 (s, 3 H, CH_3), 2.80–3.98 (m, 4 H,

Table III. Crystallographic Data for *meso*-5b

formula	$C_{36}H_{42}P_2(ClO_4)_2$
fw	735.6
space group	$P2_1/c$
molecules/unit cell	4
unit-cell dimens at 20 °C	
a	10.4905 (11) Å
b	21.694 (3) Å
c	16.571 (2) Å
β	105.53 (1)°
V	3633.6 Å³
D_{calcd} (at 20 °C)	1.345 g·cm^{-3}
D_{measd}	1.337 g·cm^{-3} (aq soln of KI)
radiation unit cell	Cu Kα_1, λ = 1.54051 Å
intensity data	Cu K$\bar{\alpha}$, λ = 1.5418 Å
scan mode	θ–2θ
$2\theta_{max}$	150°
scan angle	(0.70 + 0.14 tan θ)°
aperture width	(3.0 + 0.86 tan θ) mm
max scan time	50 s
total no. of reflctns	7422
no. of unobserved $I < 2\sigma(I)$	2189
μ(Cu K$\bar{\alpha}$)	28.4 cm^{-1}
cryst dimens	0.48 × 0.19 × 0.09 mm

PCH_2CH_2) 4.73 (t, J_{PCH} = 13.5 Hz, 2 H, PCH_2P), 7.42–8.04 (m, 20 H, ArH and PH); ^{1}H-decoupled ^{31}P NMR (Me_2SO-d_6) +21.24 (d, J_{PCP} = 10.6 Hz, P^+), +30.03 ppm (d, J_{PCP} = 10.6 Hz, P^+–H).

Anal. Calcd for $C_{30}H_{32}P_4F_{12}$: C, 48.40; H, 4.33; P, 16.64. Found: C, 48.26; H, 4.48; P, 16.47.

1,1′-(Methanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Bis[hexafluorophosphate(1−)] (18). The dibromide **16** (0.5 g, 0.007 mol) was cyclized by the use of 40 g of 115% PPA at 205 °C following the general procedure. Reprecipitation (H_2CCl_2–ether) of crude salt gave 0.15 g (26%) of **18**: mp 165–168 °C; IR (KBr) ν 1438, 1110, 994, 844, 745, 692 cm^{-1}; ^{1}H NMR ($DCCl_3$–TFA, 20:1) δ 0.99–1.40 (m, 12 H, CH_3), 1.48–3.62 (m, 10 H, CH_2), 7.12–7.96 (m, 18 H, ArH); ^{1}H-decoupled ^{31}P NMR ($DCCl_3$–TFA, 20:1) +10.01, +11.25 ppm.

Anal. Calcd for $C_{35}H_{40}P_4F_{12}$: C, 51.74; H, 4.96; P, 15.25. Found: C, 51.53; H, 5.06; P, 15.09.

Alkaline Hydrolysis of *meso*-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Dichloride (*meso*-5a). Aqueous sodium hydroxide (10 mL, 2 N) was added to a solution of *meso*-**5a** (2.0 g, 0.0033 mol) in 50 mL of H_3COH, and the mixture was boiled for 3 h. The cooled reaction mixture was diluted with water (200 mL) and extracted with benzene (3 × 50 mL). The extract was dried (Na_2SO_4) and treated with 3 mL of H_3CI. The mixture was allowed to stand overnight at room temperature. The solid separated was filtered and reprecipitated (H_2CCl_2–ether) to give 0.98 g (75%) of the methiodide **27**, mp 198–200 °C. The methiodide **27** was characterized as the hexafluorophosphate **28** which was prepared by treating 0.5 g (0.00125 mol) of **27** in 20 mL of H_3COH–H_2O (1:1) with 20 mL of saturated aqueous KPF_6. The mixture was stirred for 30 min. The solid formed was collected by filtration and dissolved in H_2CCl_2 (ca. 15 mL). The solution was dried (Na_2SO_4), and excess (25 mL) ether was added until the solution became cloudy. After a period of 2 h, a solid separated which was filtered and reprecipitated (H_2CCl_2–ether) twice to yield 0.43 g (83%) of **28**, mp 211–213 °C [lit.[11b] mp 211–213.5 °C]. The benzene filtrate, after separation of methiodide **27**, was evaporated, and the yellow oil obtained was chromatographed on silica gel (benzene). The resulting oil was stored in a refrigerator for a period of 3 days. The waxy solid obtained was recrytallized (hexane) to give 0.4 g (45%) of phosphine oxide **29**, mp 107–108 °C [Lit.[11c] mp 99–101 °C].

Anal. Calcd for $C_{16}H_{19}PO$: m/e (M^+) 270.1173. Found: m/e 270.1163.

Lithium Aluminum Hydride Reduction of *meso*-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Dichloride (*meso*-5a). Lithium aluminum hydride (0.125 g, 0.0033 mol) and *meso*-**5a** (0.4 g, 0.00066 mol) were stirred under reflux in dry THF (25 mL) for a period of 24 h. The reaction mixture was cooled to room temperature, and the excess hydride was destroyed by *careful* addition of ice-cold water (ca. 2.5 mL). The reaction mixture was extracted with ether (3 × 25 mL). The extract was dried (Na_2SO_4), concentrated to ca. 10 mL, and treated with H_3CI (2 mL). The mixture was allowed to stand overnight in refrigerator. The solid separated was filtered and reprecipitated (H_2CCl_2–ether) to give 0.16 g (31%) of **27**, mp 198–200 °C. A small amount of the methiodide **27** was converted to the hexafluorophosphate **28**, mp 211–213 °C (lit.[11b] mp 211–213.5 °C).

Sodium Hydride Reduction of *meso*-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Dichloride (*meso*-5a). A suspension of *meso*-**5a** (0.607 g, 0.001 mol) and sodium hydride (0.048 g, 0.002 mol, 50% dispersion in paraffin washed with dry ether) in THF (20 mL, distilled from $LiAlH_4$) was stirred at room temperature for a period of 12 h. The reaction mixture was filtered directly into a large excess of H_3CI (5 mL) in ether (20 mL). The solid formed was filtered and reprecipitated (H_2CCl_2 and ether) to give 0.0115 g (15%) of **27**, mp 198–200 °C. A small amount (0.075 g) of the methiodide **27** was converted to **28**, mp 211–213 °C (lit.[11b] mp 211–213.5 °C).

Crystallographic Experimental Data. A plate shaped crystal of dimensions 0.48 × 0.19 × 0.09 mm was selected for all X-ray measurements. Early investigation showed the crystal to be monoclinic. Systematic absences uniquely determined the space group to be $P2_1/c$. The crystal data of *meso*-**5b** are given in Table III.

The cell parameters were determined by least-squares fit to $+2\theta$ and -2θ values of 48 reflections measured at 20 °C by using Cu Kα_1 radiation. The density was determined by flotation in aqueous solution of potassium iodide.

Intensities of all unique reflections with 0° < 2θ < 150° were measured at 20 °C using Ni-filtered Cu K$\bar{\alpha}$ radiation on an Enraf-Nonius CAD-4 counter diffractometer. The θ–2θ scan technique was employed by using a variable scan speed. The relevant data collection parameters

Table IV. Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters for Nonhydrogen Atoms[a]

	x	y	z	U_{eq}, Å²
Cl(1)	8956.9 (9)	3884.3 (4)	2539.0 (5)	0.0602 (5)
Cl(2)	5629.6 (9)	1507.3 (4)	2860.4 (6)	0.0597 (5)
P(1)	4708.0 (8)	3203.1 (3)	695.9 (5)	0.0407 (4)
P(1)′	8058.4 (8)	2249.0 (4)	245.2 (5)	0.0481 (4)
C(2)	5010 (3)	3182 (1)	1805 (2)	0.0499 (16)
C(3)	3781 (4)	3441 (2)	2016 (2)	0.0591 (20)
C(4)	3541 (3)	4131 (2)	1831 (2)	0.0555 (18)
C(4a)	3453 (3)	4292 (1)	917 (2)	0.0459 (15)
C(5)	2881 (3)	4854 (1)	597 (2)	0.0608 (19)
C(6)	2793 (4)	5041 (2)	−213 (3)	0.0675 (20)
C(7)	3303 (4)	4681 (2)	−734 (2)	0.0627 (19)
C(8)	3889 (3)	4124 (2)	−451 (2)	0.0533 (17)
C(8a)	3951 (3)	3929 (1)	374 (2)	0.0412 (14)
C(9)	6239 (3)	3155 (1)	395 (2)	0.0497 (16)
C(10)	4677 (4)	4514 (2)	2394 (2)	0.0808 (25)
C(11)	2233 (4)	4293 (2)	2045 (3)	0.0896 (29)
C(12)	3692 (3)	2569 (1)	216 (2)	0.0459 (15)
C(13)	3646 (4)	2035 (2)	658 (2)	0.0747 (23)
C(14)	2933 (5)	1533 (2)	275 (3)	0.0878 (26)
C(15)	2226 (4)	1562 (2)	−548 (3)	0.0816 (25)
C(16)	2281 (5)	2086 (2)	−995 (3)	0.1010 (29)
C(17)	2991 (4)	2591 (2)	−614 (2)	0.0875 (25)
C(2)′	6935 (4)	1758 (2)	−483 (2)	0.0634 (20)
C(3)′	6561 (4)	1221 (2)	18 (3)	0.0774 (24)
C(4)′	7713 (5)	786 (2)	433 (3)	0.0830 (25)
C(4a)′	8969 (4)	1115 (2)	944 (2)	0.0741 (24)
C(5)′	9982 (5)	760 (2)	1479 (3)	0.1059 (32)
C(6)′	11138 (5)	1021 (3)	1935 (3)	0.1148 (35)
C(7)′	11354 (4)	1645 (2)	1918 (3)	0.1011 (32)
C(8)′	10389 (4)	2009 (2)	1400 (2)	0.0751 (24)
C(8a)′	9221 (3)	1744 (2)	914 (2)	0.0595 (19)
C(9)′	7145 (3)	2643 (1)	870 (2)	0.0461 (15)
C(10)′	8075 (6)	383 (2)	−240 (3)	0.1129 (36)
C(11)′	7147 (6)	362 (2)	1006 (4)	0.1206 (38)
C(12)′	8838 (3)	2811 (2)	−254 (2)	0.0515 (17)
C(13)′	9324 (3)	3352 (2)	164 (2)	0.0606 (19)
C(14)′	9889 (4)	3799 (2)	−238 (3)	0.0744 (23)
C(15)′	9967 (4)	3697 (2)	−1043 (3)	0.0861 (27)
C(16)′	9493 (4)	3166 (2)	−1448 (3)	0.0913 (29)
C(17)′	8919 (4)	2713 (2)	−1066 (2)	0.0719 (23)
O(1)	9648 (3)	3356 (1)	2359 (2)	0.0987 (20)
O(2)	9795 (4)	4248 (2)	3102 (3)	0.1516 (29)
O(3)	8340 (6)	4142 (2)	1806 (2)	0.2072 (43)
O(4)	7971 (4)	3670 (2)	2905 (3)	0.1527 (34)
O(5)	5123 (4)	2033 (1)	3183 (2)	0.1141 (23)
O(6)	4553 (3)	1131 (2)	2445 (2)	0.1146 (22)
O(7)	6319 (3)	1706 (1)	2283 (2)	0.0886 (18)
O(8)	6454 (3)	1173 (1)	3532 (2)	0.0870 (18)

[a] Standard deviations of the last digits are in parentheses. $U_{eq} = 1/(6\pi^2)\Sigma\Sigma b_{ij}\bar{a}_i\bar{a}_j$.

are listed in Table III. Intensities of three reflections were monitored after every 2 h of X-ray exposure. All intensity data were corrected for Lorentz and polarization factors. A Gaussian method[31] was employed to make the absorption correction by using 216 sampling points. Each structure amplitude was assigned a weight, $\omega_F = 1/\sigma_{F^2}$, where σ_F was obtained from counting statistics.[32]

The positions of the two chlorine and two phosphorus atoms were obtained from an E map evaluated by using the direct methods program MULTAN.[33] The remainder of the structure was obtained by successive difference Fourier syntheses. All hydrogen atoms were located from a difference Fourier map calculated at a later stage of least-squares refinement. All nonhydrogen atoms were given anisotropic thermal parameters, while the hydrogen atoms were refined isotropically. In the final cycles of refinement, the anomalous dispersion effects of Cu-radiation by Cl and P atoms were taken into account. Refinement was terminated when the maximum parameter shifts of the nonhydrogen atoms were less than 40% of their corresponding standard deviation. The final R factor for 5056 reflections included into the least-squares calculations is 0.054, while it is 0.091 for all 7433 reflections. All refinements were carried out by using a block diagonal least-squares method,[34] in which the quantity, $\sum o(kF_o - F_c)^2$, was minimized. Scattering factors for Cl, P, O, and C were taken from ref 35 while those of the hydrogen atoms were from Stewart, Davidson, and Simpson (1965).[36]

The final positional parameters along with equivalent isotropic thermal parameters for all nonhydrogen atoms are given in Table IV.

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Registry No. *meso*-**5a**, 80799-76-4; *meso*-**5b**, 80799-73-1; **6a**, 1663-45-2; **6b**, 6737-42-4; **6c**, 7688-25-7; **6d**, 27721-02-4; **6e**, 19845-69-3; **7a**, 81194-90-3; **7b**, 81194-91-4; **7c**, 81194-92-5; **7e**, 81194-93-6; **8a**, 81194-95-8; **8b**, 81194-97-0; **8c**, 81194-99-2; **8d**, 81195-01-9; **8e**, 81195-03-1; **9a**, 81195-05-3; **9b**, 81195-07-5; **9c**, 81195-09-7; **9d**, 81195-11-1; **9e**, 81195-13-3; **10**, 2071-20-7; **11**, 81195-14-4; **12**, 81195-16-6; **13**, 81205-74-5; **16**, 81195-17-7; **17**, 81195-19-9; **18**, 81195-21-3; **27**, 81195-22-4; **28**, 56771-37-0; **29**, 58191-14-3; 1-chloro-3-methyl-2-butene, 503-60-6; 1-bromo-3-methyl-2-butene, 870-63-3; 3-bromopropene, 106-95-6; 5-bromo-1-pentene, 1119-51-3; 4-bromo-1-butene, 5162-44-7; **19**, 81195-24-6; **21**, 81195-26-8; **23**, 81195-28-0.

Supplementary Material Available: A listing of anisotropic thermal parameters and hydrogen atom parameters (4 pages). Ordering information is given on any current masthead page.

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Carbon–Phosphorus Heterocycles. Synthesis, Separation, and Resolution of Stereoisomers of 1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Diperchlorate. The Use of ^{31}P NMR Analysis To Monitor the Resolution

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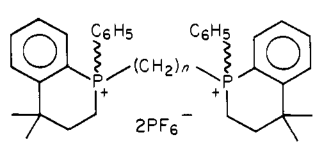
Abstract: The synthesis of the diastereomeric mixture of the title compound via polyphosphoric acid induced intramolecular alkylation of a strategically designed, open-chain precursor was recorded for the first time. The meso and (±) diastereomers were separated by fractional crystallization, and partial resolution of the (±) form was attained via the use of Ag hydrogen dibenzoyltartrates [L(+) and D(−)]. The ^{31}P NMR analysis was advantageously used to monitor the separation of diastereomers and the resolution of (±) form. Spectral data for all of the stereoisomers has been briefly discussed for these first members of the title compounds. Evidence is presented which strongly suggests that nonequivalence at phosphorus is induced in the meso isomer via the presence of a chiral anion such as hydrogen dibenzoyltartrate. The separation and resolution are the first recorded in this family of heterocycles also.

The preceding paper[1] described the synthesis of 1,1′-(α,ω-alkanediyl)bis(1,2,3,4-tetrahydrophosphinolinium) salts **1** (n = 1–6)



1

which were dissymmetric because of the presence of two asymmetric phosphorus atoms in the two rings. A search of the literature revealed that only simple C–P heterocycles containing one asymmetric phosphorus atom have been resolved into optical antipodes.[2-6] The first and *only* previous successful separation of diastereomers and resolution of an *open-chain* bis(phosphonium) salt **2** was recorded by Horner and co-workers.[7] Heretofore, no heterocyclic bis(phosphonium) salt containing two asymmetric phosphorus atoms in two rings has been separated into diastereomers or resolved into optical antipodes.[8] We report herein

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