trihydrate (0.47 g, 0.19 mmol) in 2-propanol (30 cm^3) was treated with $Bu^t{}_2P(CH_2)_6PBu^t{}_2$ (1.06 g, 2.34 mmol) and the mixture was heated under reflux for 20 h. The resultant orange solution when cooled gave the required product which formed orange needles from light petroleum (bp 60-80 °C), yield 0.45 g (0.088 mmol, 47%).

$[RhCl\{Bu^t{}_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t{}_2\}]$ from $Bu^t{}_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t{}_2$. A solution of rhodium trichloride trihydrate (0.52 g, 2.09 mmol) in a mixture of water (2 cm^3) and 2-propanol (10 cm^3) was treated with a solution of $Bu^t{}_2P(CH_2)_2CH{=}CH(CH_2)_2PBu^t{}_2$ (1.17 g, 3.13 mmol) in benzene (3 cm^3). The mixture was refluxed for 7 days. The resultant yellow solution was evaporated to a glassy solid and then extracted with light petroleum (bp 60-80 °C). The required product (0.28 g, 27%) separated on cooling.

$[Rh(CO)\{Bu^t{}_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t{}_2\}]ClO_4$. Carbon monoxide was bubbled through a solution of the chloro complex (0.19 g, 0.38 mmol) in ethanol (ca. 20 cm^3) to which had been added a solution of sodium perchlorate monohydrate (0.25 g, 1.78 mmol) in water (0.5 cm^3). After 2 h water was slowly added to the resultant yellow solution to give the required perchlorate complex as yellow needles, yield 0.21 g (0.34 mmol, 92%).

$[Rh(CO)\{Bu^t{}_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t{}_2\}]BPh$. This was prepared similarly to the perchlorate (above) using an ethanol solution of sodium tetraphenylboron (fourfold excess). The product formed yellow microcrystals, yield 90%.

Action of $Bu^t{}_2PCH_2CH{=}CHCH_2PBu^t{}_2$ on Rhodium Trichloride. A solution of rhodium trichloride trihydrate (0.23 g, 0.89 mmol) in water (1 cm^3) and 2-propanol (25 cm^3) was treated with a solution of the diphosphine (0.68 g, 1.96 mmol) in 2-propanol (13 cm^3). A pinkish-brown precipitate was produced which had all dissolved after boiling the mixture for 3 h. The orange solution was filtered and the solvent removed at the pump to give an orange oil. Water (15 cm^3) was added and the precipitated yellow solid (0.35 g, 81%) filtered off. The product was recrystallized from dichloromethane-cyclohexane.

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Crystal Structures of Some Cyclic Phosphonium Salts and Their Relation to the Stereochemical Course of Base Hydrolysis

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Abstract: Single-crystal X-ray analyses of 1-benzyl-1-phenylphosphorinanium bromide (I) and 1,1-diphenyl-4-methylphosphorinanium bromide (II) showed that their structures are very similar. Each contains the six-membered ring in the chair form and in the case of I the benzyl group is oriented equatorially at the tetrahedral phosphorus atom. I crystallizes in the monoclinic space group Cc with a = 16.666 (5) Å, b = 9.690 (4) Å, c = 11.806 (2) Å, β = 114.42 (2)°, and Z = 4. Full-matrix least-squares refinement gave R = 0.033 and R_w = 0.035 for the 1713 reflections having $I \geq \sigma(I)$. II crystallizes in the monoclinic space group $C2/c$ with a = 15.199 (4) Å, b = 10.986 (2) Å, c = 21.212 (8) Å, β = 99.71 (3)°, and Z = 8. Full-matrix least-squares refinement gave R = 0.40 and R_w = 0.042 for the 3100 reflections having $I \geq \sigma(I)$. The X-ray coordinates of I were used to initiate a molecular mechanics calculation designed to simulate base hydrolysis of the cis and trans isomers of 1-benzyl-1-phenyl-4-methylphosphorinanium bromide. The results support less inversion of configuration for the trans isomer compared to that for the cis isomer in accord with experimental results.

Introduction

The hydrolysis reactions of phosphonium salts represent widely studied systems.[2] In the absence of unusual steric effects[3] or departing groups of similar apicophilicity, chiral acyclic phosphonium salts hydrolyze with inversion of configuration.[4] For cyclic derivatives, ring size becomes an important determinant of reaction stereospecificity and reaction rate. For example, a comparison of the rates of alkaline de-

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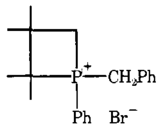
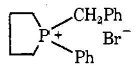
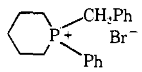
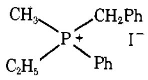
Table I. Rates of Hydrolysis for Phosphonium Salts

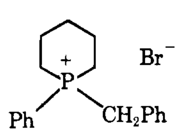
	k_3 at 25 °C[a]
	2.77×10^{3} [b]
	0.171[b]
	1.59×10^{-3} s^{-1} [c]
	3.29×10^{-4} [b]

[a] Rate coefficient is third order (L^2 mol^{-2} s^{-1}). The benzyl group is the leaving group in all cases. [b] See ref 5. Solvent system was 1:1 EtOH-H_2O (v/v) at 25 °C. [c] A value of 5.6×10^{-4} L^2 mol^{-2} s^{-1} from ref 5 was found to be reproducible but not associated with oxide formation.[6b] The value listed above is a pseudo-first-order rate constant more recently determined (see ref 6b).

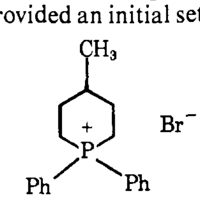
composition of the phosphonium salts determined by Cremer and co-workers[5] (Table I) shows that the four-membered-ring derivative reacts faster than the one with the five-membered ring and the latter apparently reacts faster than the six-membered-ring derivative. The rate order has been explained in terms of relief of ring strain on forming a trigonal-bipyramidal transition state where the four- or five-membered ring spans apical–equatorial sites. Here the departing benzyl group is not in the favored apical leaving position and pseudorotation is postulated, leading to a retention pathway. The six-membered ring may span diequatorial positions more easily and, as the comparable rate to the related acyclic derivative suggests, an inversion pathway may also be possible.

However, as with acyclic derivatives, introduction of substituents producing steric effects may cause some reactions of cyclic phosphonium salts to lack stereospecificity. Marsi and Clark[6a] found the product stereochemistries listed in Table II for the alkaline cleavage of 1-phenyl-1-benzyl-4-methylphosphorinanium salts reflecting both the inversion and retention pathways. A similar study on the 1-phenyl-1-benzyl-4-*tert*-butylphosphorinanium salts also supports the dual mechanism for hydrolysis.[6b] Incorporating a better departing group, OCH_3, the inversion process takes over.[7]

In order to understand the detailed operation of steric and ring-strain effects in determining the course of alkaline hydrolysis of phosphorinanium salts, we undertook the X-ray structural analyses of the two six-membered ring compounds, I and II. The structural results provided an initial set of coor-



I



II

dinates that was incorporated in a molecular mechanics approach used to model the hydrolysis reaction for the cis and trans isomers of 1-benzyl-1-phenyl-4-methylphosphorinanium bromide. The inversion mechanism for both chair forms for each isomer was investigated upon approach of hydroxide ion opposite the benzyl group. By doing so, we were able to obtain a reaction profile of the hydrolysis process which correlated with the results of Table II and those in the succeeding article,[8] both in terms of ring-size effects and product differences encountered from use of cis and trans isomers.

Experimental Section

Preparation of I. 1-Benzyl-1-phenylphosphorinanium bromide was prepared by a two-step synthesis reported by Cremer, Trivedi, and Weitl.[5] This involved reaction of a di-Grignard, made from 1,5-dibromopentane, with phenylphosphorus dichloride in ether to form 1-phenylphosphorinane. The latter phosphine was subsequently reacted with benzyl bromide in ether to form the desired product. A white, crystalline solid which resulted from recrystallization from acetonitrile provided a suitable sample for the X-ray determination, mp (uncor) 185–186 °C. Anal. Calcd for $C_{18}H_{22}BrP$: C, 61.90; H, 6.35; Br, 22.88; P, 8.87. Found: C, 61.64; H, 6.35; P, 8.60.

Preparation of II. 1,1-Diphenyl-4-methylphosphorinanium bromide was synthesized by Märkl's procedure[9] involving the addition of 3-methyl-1,5-dibromopentane to tetraphenyldiphosphine in *o*-dichlorobenzene. Recrystallization from acetonitrile gave suitable crystals for X-ray analysis, mp (uncor) 285–286 °C. Anal. Calcd for $C_{18}H_{22}BrP$: C, 61.90; H, 6.35; Br, 22.88; P, 8.87. Found: C, 61.73; H, 6.39; Br, 22.92.

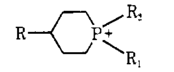
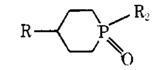
Space-Group Determination and Data Collection for I. Preliminary precession photographs recorded with Cu Kα radiation revealed a monoclinic system (Laue symmetry $2/m$) with the following systematic absences: hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$. The space-group possibilities were restricted to Cc and $C2/c$. A colorless crystal of dimensions $0.29 \times 0.20 \times 0.20$ mm was sealed in a thin-walled glass capillary. The crystal was mounted on an Enraf-Nonius CAD 4 automated diffractometer. Using graphite-monochromated Mo K$\bar{\alpha}$ radiation (fine focus tube, 45 kV, 20 mA, take-off angle = 3.1°, $\lambda K_{\alpha 1}$ = 0.709 26 Å, $\lambda K_{\alpha 2}$ = 0.713 54 Å) unit-cell constants and an orientation matrix were determined by a least-squares refinement of the diffraction geometry for 25 reflections with $10.03° \leq \theta_{MoK\bar{\alpha}} \leq 15.01°$ measured at ambient temperature. From the unit-cell volume of 1736.0 (1.8) Å^3 and the assumption that each nonhydrogen atom occupies about 20 Å^3, Z was calculated as 4 and the space group Cc was chosen [C^4s; no. 9].[10] Further refinement in Cc showed that this choice was correct. The lattice constants are a = 16.666 (5) Å, b = 9.690 (4) Å, c = 11.806 (2) Å, β = 114.42 (2)°. The calculated density for a unit cell content of four molecules is 1.34 g/cm^3.

Data were collected using the coupled ω–2θ scan mode, with a 2θ scan range of $(0.85 + 0.35 \tan \theta)°$ centered about the calculated Mo K$\bar{\alpha}$ peak position. The scan range was actually extended an extra 25% on both sides of the latter limits for the measurement of background radiation. The scan rates varied from 0.48 to 4.02°/min, the rate to be used for each reflection having been determined by a prescan. The intensity, I, for each reflection is thus given by $I = (FF/S)[P - 2(B_1 + B_2)]$, where P is the count accumulated during the peak scan, B_1 and B_2 are the left and right background counts, S is an integer inversely proportional to the scan rate, and FF is either unity or a multiplier to account for the attenuation of the diffracted beam. The standard deviations in the intensities, $\sigma(I)$, were computed as $\sigma(I)^2 = (FF/S)^2[P + 4(B_1 + B_2)] + 0.002I^2$.

A total of 1983 independent reflections ($+h$, $+k$, $\pm l$) with $2° \leq 2\theta_{MoK\bar{\alpha}} \leq 55°$ was measured in two concentric shells. The first shell contained 988 reflections and the second 995. Six standard reflections, monitored after every 12 000 s of X-ray exposure time, gave no indication of crystal deterioration or loss of alignment. The intensities were reduced to relative amplitudes, F_o, by means of standard Lorentz and polarization corrections. The 1772 reflections with intensities greater than $0.2\sigma(I)$ were treated as observed. Reflections for which $I \leq 0.2\sigma(I)$ were assigned $F_o = [c\sigma(I)/Lp]^{1/2}$ and $\sigma(F_o) = 0.5F_o/c$, where L_p is the Lorentz-polarization factor and $c = 0.2$. Owing to the large linear absorption coefficient, $\mu_{MoK\bar{\alpha}}$ = 25.9 cm^{-1}, an absorption correction was applied toward the end of the refinement. The Gaussian grid method was used and resulted in maximum and minimum transmission coefficients of 0.69 and 0.55. Application of the absorption correction did not cause any significant changes in the bond lengths or angles. Also, toward the end of the refinement, an anomalous dispersion correction was applied for P and Br^-;[11] the correction terms for the bromide ion were assumed to be the same as those for bromine.

Solution and Refinement of the Structure for I. Computations were done on a CDC 6600 computer, Model Cyber 74-18, using Zalkin's Fourier program FORDAP, Prewitt's full-matrix least-squares program SFLS5, Johnson's thermal ellipsoid plot program ORTEP, and several locally written programs. Bond lengths, angles, and standard deviations were obtained using ORFFE. The scattering factors for all nonhydrogen atoms were taken from Cromer and Waber;[12] scattering

Table II. Product Stereochemistry for Alkaline Cleavage of Phosphorinanium Salts[a]

			compd 		product 		
entry		R	R_1	R_2	retention[b]	inversion	ref
1	cis	CH_3	CH_2Ph	Ph	48	52	6a
2	trans	CH_3	CH_2Ph	Ph	78	22	6a
3	cis	*t*-Bu	CH_2Ph	Ph	66	34	6b
4	trans	*t*-Bu	CH_2Ph	Ph	79	21	6b
5	cis	CH_3	OCH_3	Ph	0	100	7
6	trans	CH_3	OCH_3	Ph	0	100	7

[a] Cis and trans refer to the orientation of R_2 and R. However, when methoxy is present, cis and trans refer to methoxy and R group orientation. [b] Retention describes reactant-product geometry, cis-cis and trans–trans; inversion refers to cis-trans and trans-cis changes.

factors for the hydrogen atoms were taken from Stewart et al.[13] The function minimized by the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2LpF_o/\sigma(I)$.

The three-dimensional Patterson function was used to locate the bromide ion y position. The x and z coordinates were chosen arbitrarily and then fixed during least-squares refinement for origin definition. The difference Fourier map, phased on the bromide ion, revealed the positions of all the remaining nonhydrogen atoms.

Refinement of these structural parameters for the 20 nonhydrogen atoms and a scale factor using isotropic (bromide ion and phosphorus are anisotropic) full-matrix least-squares with experimental weights gave a conventional residual $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.048 and a weighted residual $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$ of 0.064 for the 964 reflections with $\sin\theta/\lambda \leq 0.52$ and $I \geq 3\sigma(I)$. For these same reflections, anisotropic refinement gave $R = 0.038$ and $R_w = 0.052$. A difference Fourier was run and all 22 hydrogen atoms appeared.

Initial coordinates for the 22 independent hydrogen atoms were calculated from the required molecular geometry. Further refinement with the hydrogen atoms as isotropic contributions gave $R = 0.024$ and $R_w = 0.029$ for these 964 reflections. The final cycles of refinement included the high-angle data with the absorption and anomalous dispersion corrections given above and resulted in $R = 0.033$, $R_w = 0.035$, and GOF (goodness of fit)[14] = 1.038 and for 1713 reflections with $I \geq \sigma(I)$ and $2° \leq 2\theta_{MoK\bar{\alpha}} \leq 55°$.[15]

During the final cycle of refinement the largest shift in any parameter was 0.08 times its estimated standard deviation. A final difference Fourier synthesis (1713 reflections) showed a maximum density of 0.54 e/Å^3. A structure-factor calculation using the final refined parameters and including the weak data (a total of 1983 reflections) gave $R = 0.046$ and $R_w = 0.035$; a difference Fourier based on this set showed a maximum electron density of 0.60 e/Å^3.

Space-Group Determination and Data Collection for II. A crystal of dimensions 0.250 × 0.300 × 0.375 mm was sealed in a glass capillary for the X-ray diffraction study. Conditions for data collection on the CAD-4 diffractometer and data reduction were the same as given for I, except that the scan range was $(0.75 + 0.35 \tan\theta)°$. Reflections for which $I \leq 0.2\sigma(I)$ were assigned F_o and $\sigma(F_o)$ as for I. Preliminary diffractometric investigation indicated monoclinic symmetry ($2/m$). From the observed extinctions hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, the space-group possibilities were restricted to Cc and $C2/c$. From the measured volume of 3491 Å^3 and the assumption that each nonhydrogen atom occupies about 20 Å^3, Z was calculated to be 8. Thus, the space group $C2/c$[16] was assumed as the correct one. The lattice constants as determined by the least-squares refinement of the diffraction geometry for 25 reflections having $10.36° \leq \theta_{MoK\bar{\alpha}} \leq 16.25°$ are $a = 15.199$ (4) Å, $b = 10.986$ (2) Å, $c = 21.212$ (8) Å, and $\beta = 99.71$ (3)°. A unit-cell content of eight molecules gives a calculated density of 1.33 g/cm^3, almost exactly that obtained for I.

A total of 4008 independent reflections ($\pm h$, $+k$, $+l$) with $2° \leq 2\theta_{MoK\bar{\alpha}} \leq 55°$ were measured in two concentric shells of increasing 2θ. An absorption correction was not applied here, even though the linear absorption coefficient was large: $\mu_{MoK\bar{\alpha}} = 25.8$ cm^{-1}. Since the absorption correction done on I did not make any important geometrical changes (the structure had been fully refined before the correction was applied) and since the crystal used for this compound was fairly equidimensional, it was felt that an absorption correction was not necessary here. The 3263 reflections with $I > 0.2\sigma(I)$ were treated as observed. As with I, anomalous dispersion correction terms were included for P and Br^- near the end of the refinement.

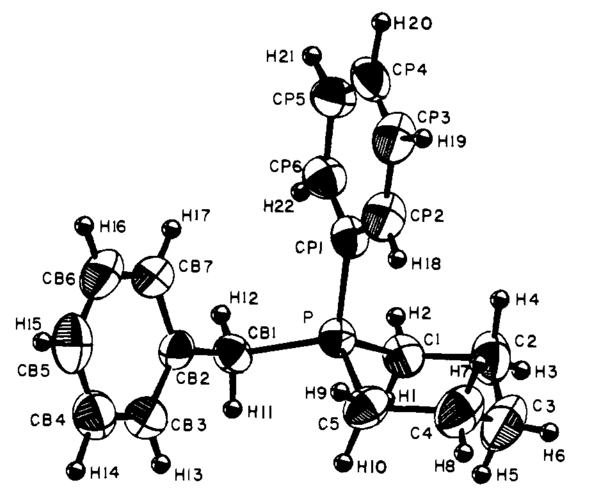


Figure 1. ORTEP plot of the $(C_5H_{10})P^+(C_6H_5)(C_7H_7)Br^-$ salt (I) with thermal ellipsoids at the 50% probability level for nonhydrogen atoms. Hydrogen atoms are represented by spheres of arbitrary radius.

Solution and Refinement of the Structure for II. Computations were carried out similar to those for I except that the full-matrix least-squares program LINEX was used near the end of refinement. This is a modification of the Oak Ridge program ORFLS.

The three-dimensional Patterson function was used to locate the bromide ion position. The difference Fourier map phased on this bromide ion showed the positions of all the remaining nonhydrogen atoms. Isotropic, unit weighted, full-matrix least-squares refinement of the structural parameters (P and Br^- atoms were anisotropic) and one scale factor gave $R = 0.056$ and $R_w = 0.062$ for the 1697 reflections with $I \geq 3\sigma(I)$ and $\sin\theta/\lambda \leq 0.52$. Anisotropic refinement for these same reflections gave $R = 0.047$ and $R_w = 0.055$. At this point, a difference Fourier map gave geometrically reasonable coordinates for only one of the three methyl hydrogens. The initial coordinates for the remaining 21 hydrogens were calculated from the required geometry of the molecule.

The methyl hydrogens did not refine properly, and it was necessary to fix their initial coordinates and thermal parameters. The final refinement cycles were done with variable weights and the anomalous dispersion correction, and resulted in $R = 0.040$, $R_w = 0.042$, and GOF[17] = 1.179 for the 3100 reflections with $I > \sigma(I)$ and $2° \leq 2\theta_{MoK\bar{\alpha}} \leq 55°$. During the final cycle of refinement, the largest shift for any parameter was 0.01 times its estimated standard deviation. A final difference Fourier synthesis using the 3100 reflections showed a maximum density of 0.50 e/Å^3. Further refinement of the final parameter set using all 4008 reflections resulted in $R = 0.060$ and $R_w = 0.043$, while a difference Fourier based on this parameter set showed a maximum density of 0.52 e/Å^3.

Results and Discussion

Figures 1 and 2 show the molecular geometry of I and II and their respective atom labeling schemes. Atomic coordinates

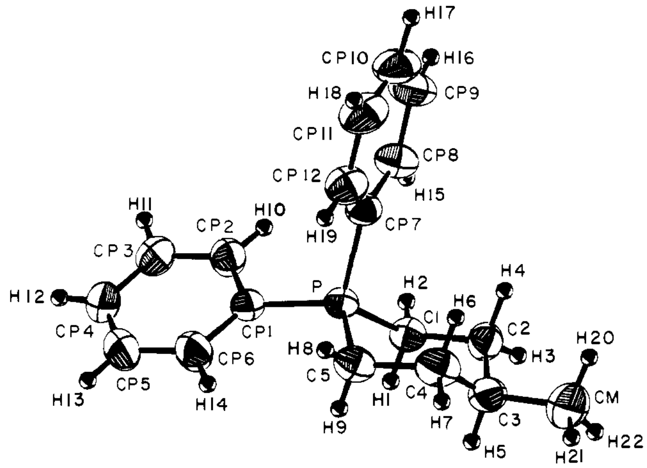


Figure 2. ORTEP plot of the $(C_5H_9(CH_3))P^+(C_6H_5)_2Br^-$ salt (II) with thermal ellipsoids at the 50% probability level for nonhydrogen atoms. Hydrogen atoms are represented by spheres of arbitrary radius.

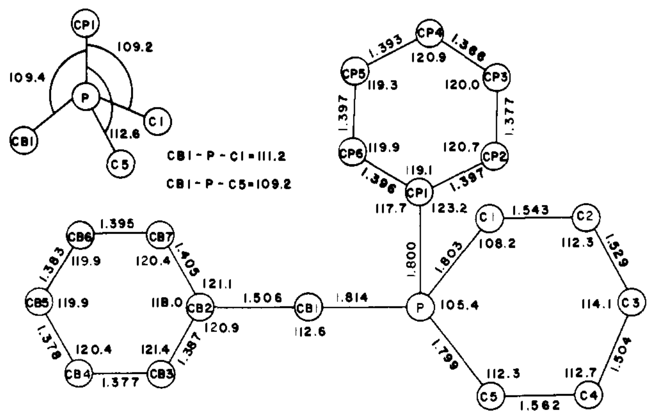


Figure 3. Schematic diagram of $(C_5H_{10})P^+(C_6H_5)(C_7H_7)Br^-$ (I) illustrating bond parameters (lengths, Å; angles, deg).

Table III. Atomic Coordinates in Crystalline $(C_5H_{10})P^+(C_6H_5)$-$(C_7H_7)Br^-$ (I) with Standard Deviations in Parentheses

atom[a]	10^4x	10^4y	10^4z
Br	0 (fixed)	265.4(4)	0 (fixed)
P	3532.9(8)	2822.1(11)	1636.4(11)
C1	3401(3)	4670(5)	1504(5)
C2	2443(4)	5019(6)	1276(7)
C3	2220(5)	4548(8)	2348(8)
C4	2199(4)	3007(8)	2484(8)
C5	3105(4)	2313(7)	2745(5)
CP1	2940(3)	2053(4)	131(4)
CP2	2189(3)	1240(5)	−161(6)
CP3	1742(3)	719(6)	−1343(6)
CP4	2037(3)	984(6)	−2242(6)
CP5	2802(4)	1750(6)	−1975(5)
CP6	3245(3)	2311(5)	−787(5)
CB1	4686(3)	2339(5)	2222(5)
CB2	4830(3)	821(5)	2508(4)
CB3	5152(4)	346(7)	3724(6)
CB4	5285(4)	−1040(7)	3996(6)
CB5	5100(4)	−1994(6)	3055(7)
CB6	4776(4)	−1559(6)	1831(6)
CB7	4650(4)	−155(6)	1553(5)

[a] Atoms labeled to agree with Figure 1.

appear in Tables III and IV. Thermal parameters and refined parameters for hydrogen atoms are provided as supplementary material. Bond lengths and angles are given in Table V for I and Table VI for II. Selected bond parameters are shown schematically in Figures 3 (for I) and 4 (for II).

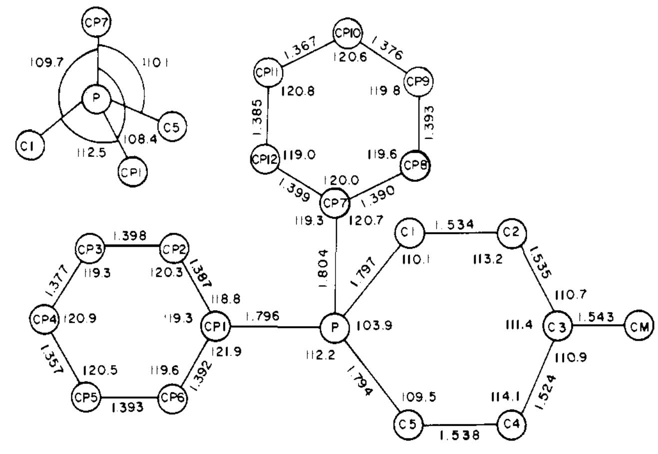


Figure 4. Schematic diagram of $(C_5H_9(CH_3))P^+(C_6H_5)_2Br^-$ (II) illustrating bond parameters (lengths, Å; angles, deg).

Table IV. Atomic Coordinates in Crystalline $(C_5H_9(CH_3))$-$P^+(C_6H_5)_2Br^-$ (II) with Standard Deviations in Parentheses

atom[a]	10^4x	10^4y	10^4z
Br	696.3(2)	2670.6(3)	817.9(2)
P	3446.8(5)	832.2(6)	882.0(3)
CP1	2755(2)	−44(2)	277(1)
CP2	1844(2)	−93(3)	280(1)
CP3	1288(2)	−785(3)	−176(2)
CP4	1657(2)	−1433(3)	−622(2)
CP5	2546(3)	−1382(4)	−635(2)
CP6	3109(2)	−692(3)	−186(2)
CP7	3256(2)	314(3)	1655(1)
CP8	2613(2)	863(3)	1953(1)
CP9	2477(3)	447(4)	2550(2)
CP10	2988(3)	−495(4)	2842(2)
CP11	3614(3)	−1046(4)	2546(2)
CP12	3758(2)	−659(3)	1950(2)
C1	3225(2)	2437(2)	804(1)
C2	3910(2)	3150(3)	1278(2)
C3	4877(2)	2934(3)	1182(2)
C4	5148(2)	1607(4)	1299(2)
C5	4609(2)	708(3)	829(2)
CM1	5522(3)	3787(4)	1615(2)

[a] Atoms labeled to agree with Figure 2.

The structures of the phosphorinanium salts I and II are very similar. Both have the six-membered heterocyclic ring in the chair form. With reference to cyclohexane ring nomenclature, the benzyl group of I is located in an equatorial position. The P-C bond lengths are all very close to 1.80 Å other than the expected longer distance to the methylene group in I, 1.814 (5) Å. The magnitude and disposition of bond angles bear a close correspondence between the two structures, particularly the endocyclic ring angles in the chair conformations. The chair forms are only slightly distorted from that observed for cyclohexane. The angles between the normal to the least-squares plane through C_1, C_2, C_4, and C_5 and the normal to the plane defined by C_5, P, and C_1 are 44.5° for I (Table VII) and 47.3° for II (Table VIII). The angles for this same normal to the least-squares plane of $C_1C_2C_4C_5$ with the normal to the plane C_2, C_3, and C_4 are 56.5° for I and 55.1° for II. For the cyclohexane structure determined by electron diffraction,[18] the above dihedral angles are 49.2°. Thus, the phosphorus portion of the ring is slightly flattened.

Some differences between these ring forms for I and II are noted by comparing their torsional angles. The torsional angle C_1-C_2-C_3-C_4 of −67.5° in Figure 5a, for example, is defined as having a (−) sense, if, when looking along the C_2-C_3 bond, atom 1 must be rotated counterclockwise by less than 180° in

Table V. Bond Lengths (Å) and Angles (deg) in Crystalline $(C_5H_{10})P^+(C_6H_5)(C_7H_7)Br^-$ (I) with Standard Deviations in Parentheses[a]

	Bond Lengths		
P-C1	1.803(5)	C1-H1	0.89(4)
P-C5	1.799(5)	C1-H2	0.88(6)
P-CP1	1.800(5)	C2-H3	0.93(6)
P-CB1	1.814(5)	C2-H4	1.07(7)
C1-C2	1.543(8)	C3-H5	1.03(7)
C2-C3	1.529(12)	C3-H6	0.77(10)
C3-C4	1.504(11)	C4-H7	0.98(6)
C4-C5	1.562(8)	C4-H8	0.90(5)
CP1-CP2	1.397(6)	C5-H9	0.97(9)
CP2-CP3	1.377(8)	C5-H10	1.08(6)
CP3-CP4	1.366(9)	CB1-H11	1.02(5)
CP4-CP5	1.393(9)	CB1-H12	0.96(5)
CP5-CP6	1.397(7)	CB3-H13	0.88(5)
CP6-CP1	1.396(7)	CB4-H14	1.11(6)
CB1-CB2	1.506(7)	CB5-H15	1.01(6)
CB2-CB3	1.387(8)	CB6-H16	0.97(5)
CB3-CB4	1.377(9)	CB7-H17	0.94(7)
CB4-CB5	1.378(9)	CP2-H18	0.95(5)
CB5-CB6	1.383(9)	CP3-H19	1.12(8)
CB6-CB7	1.395(8)	CP4-H20	0.97(6)
CB7-CB2	1.405(8)	CP5-H21	1.01(5)
		CP6-H22	1.02(5)
	Bond Angles		
CP1-P-C1	109.2(2)	C2-C3-H6	109(8)
C5-P-C1	105.4(3)	H5-C3-H6	103(8)
CB1-P-C1	111.2(2)	C4-C3-H5	107(3)
C5-P-CP1	112.6(2)	C4-C3-H6	116(7)
CB1-P-CP1	109.4(2)	C3-C4-H7	110(4)
CB1-P-C5	109.2(3)	C3-C4-H8	113(3)
P-C1-C2	108.2(4)	H7-C4-H8	110(5)
C1-C2-C3	112.3(6)	C5-C4-H7	110(3)
C2-C3-C4	114.1(6)	C5-C4-H8	101(3)
C3-C4-C5	112.7(5)	C4-C5-H9	111(5)
C4-C5-P	112.3(4)	C4-C5-H10	111(3)
P-CB1-CB2	112.6(3)	H9-C5-H10	112(5)
CB1-CB2-CB3	120.9(4)	P-C5-H9	107(4)
CB3-CB2-CB7	118.0(5)	P-C5-H10	103(3)
CB2-CB3-CB4	121.4(6)	P-CB1-H11	104(3)
CB3-CB4-CB5	120.4(5)	P-CB1-H12	105(3)
CB4-CB5-CB6	119.9(6)	H11-CB1-H12	111(4)
CB5-CB6-CB7	119.9(6)	CB2-CB1-H11	111(3)
CB6-CB7-CB2	120.4(5)	CB2-CB1-H12	112(3)
CB7-CB2-CB1	121.1(4)	CB2-CB3-H13	118(3)
P-CP1-CP2	123.2(4)	CB4-CB3-H13	120(3)
CP1-CP2-CP3	120.7(5)	CB3-CB4-H14	120(3)
CP2-CP3-CP4	120.0(5)	CB5-CB4-H14	120(3)
CP3-CP4-CP5	120.9(5)	CB4-CB5-H15	120(3)
CP4-CP5-CP6	119.3(6)	CB6-CB5-H15	119(3)
CP5-CP6-CP1	119.9(5)	CB5-CB6-H16	116(3)
CP6-CP1-CP2	119.1(4)	CB7-CB6-H16	124(3)
CP6-CP1-P	117.7(3)	CB6-CB7-H17	118(4)
P-C1-H1	106(3)	CB2-CB7-H17	122(4)
P-C1-H2	106(3)	CP1-CP2-H18	116(3)
H1-C1-H2	107(4)	CP3-CP2-H18	123(3)
C2-C1-H1	117(3)	CP2-CP3-H19	106(5)
C2-C1-H2	112(4)	CP4-CP3-H19	134(5)
C1-C2-H3	104(3)	CP3-CP4-H20	127(3)
C1-C2-H4	104(4)	CP5-CP4-H20	112(3)
H3-C2-H4	115(4)	CP4-CP5-H21	123(3)
C3-C2-H3	107(3)	CP6-CP5-H21	118(3)
C3-C2-H4	114(4)	CP5-CP6-H22	120(3)
C2-C3-H5	106(4)	CP1-CP6-H22	120(3)

[a] Atoms labeled to agree with Figure 1.

Table VI. Bond Lengths (Å) and Angles (deg) in Crystalline $(C_5H_9(CH_3))P^+(C_6H_5)_2Br^-$ (II) with Standard Deviations in Parentheses[a]

	Bond Lengths		
P-C1	1.797(3)	CP12-CP7	1.399(4)
P-C5	1.794(3)	C1-H1	0.94(3)
P-CP1	1.796(3)	C1-H2	1.01(3)
P-CP7	1.804(3)	C2-H3	0.90(3)
C1-C2	1.534(4)	C2-H4	1.02(3)
C2-C3	1.535(5)	C3-H5	0.95(3)
C3-C4	1.524(5)	C4-H6	0.99(3)
C4-C5	1.538(5)	C4-H7	0.87(3)
C3-CM	1.543(5)	C5-H8	0.97(3)
CP1-CP2	1.387(4)	C5-H9	0.89 (3)
CP2-CP3	1.398(4)		
CP3-CP4	1.377(5)	CP2-H10	0.93(2)
CP4-CP5	1.357(5)	CP3-H11	0.99(3)
CP5-CP6	1.393(5)	CP4-H12	0.85(3)
CP6-CP1	1.392(4)	CP5-H13	0.93(3)
CP7-CP8	1.390(4)	CP6-H14	0.98(3)
CP8-CP9	1.393(4)	CP8-H15	1.03(3)
CP9-CP10	1.376(5)	CP9-H16	0.89(3)
CP10-CP11	1.367(5)	CP10-H17	0.94(3)
CP11-CP12	1.385(5)	CP11-H18	0.86(3)
		CP12-H19	0.92(3)
	Bond Angles		
C1-P-C5	103.9(1)	H3-C2-H4	103(2)
C1-P-CP1	112.5(1)	C3-C2-H3	110(2)
C1-P-CP7	109.7(1)	C3-C2-H4	110(2)
C5-P-CP1	112.2(1)	C2-C3-H5	106(2)
C5-P-CP7	110.1(1)	H5-C3-CM	106(2)
CP1-P-CP7	108.4(1)	C4-C3-H5	111(2)
P-C1-C2	110.1(2)	C3-C4-H6	106(2)
C1-C2-C3	113.2(3)	C3-C4-H7	104(2)
C2-C3-C4	111.4(3)	H6-C4-H7	116(3)
C2-C3-CM	110.7(3)	C5-C4-H6	110(2)
CM-C3-C4	110.9(3)	C5-C4-H7	106(2)
C3-C4-C5	114.1(3)	C4-C5-H8	110(2)
C4-C5-P	109.5(2)	C4-C5-H9	110(2)
P-CP1-CP2	118.8(2)	H8-C5-H9	108(2)
CP1-CP2-CP3	120.3(3)	P-C5-H8	113(2)
CP2-CP3-CP4	119.3(3)	P-C5-H9	106(2)
CP3-CP4-CP5	120.9(3)	CP1-CP2-H10	120(2)
CP4-CP5-CP6	120.5(3)	H10-CP2-CP3	119(2)
CP5-CP6-CP1	119.6(3)	CP2-CP3-H11	117(2)
CP6-CP1-CP2	119.3(3)	H11-CP3-CP4	124(2)
CP6-CP1-P	121.9(2)	CP3-CP4-H12	115(2)
P-CP7-CP8	120.7(2)	H12-CP4-CP5	124(2)
CP7-CP8-CP9	119.6(3)	CP4-CP5-H13	123(2)
CP8-CP9-CP10	119.8(4)	H13-CP5-CP6	116(2)
CP9-CP10-CP11	120.6(3)	CP5-CP6-H14	121(2)
CP10-CP11-CP12	120.8(3)	H14-CP6-CP1	119(2)
CP11-CP12-CP7	119.0(3)	CP7-CP8-H15	120(2)
CP12-CP7-CP8	120.0(3)	H15-CP8-CP9	120(2)
CP12-CP7-P	119.3(2)	CP8-CP9-H16	119(2)
P-C1-H1	106(2)	H16-CP9-CP10	121(2)
P-C1-H2	110(2)	CP9-CP10-H17	117(2)
H1-C1-H2	105(2)	H17-CP10-CP11	123(2)
C2-C1-H1	111(2)	CP10-CP11-H18	122(2)
C2-C1-H2	114(2)	H18-CP11-CP12	117(2)
C1-C2-H3	109(2)	CP11-CP12-H19	122(2)
C1-C2-H4	111(2)	H19-CP12-CP7	119(2)

[a] Atoms labeled to agree with Figure 2.

order to be superimposed on atom 4. These angles show the ring to be asymmetrical in I but highly symmetrical in II. A possible explanation for these different ring symmetries lies in the presence of other substituents bonded to phosphorus. When the two groups are not identical, as the benzyl and phenyl groups in compound I, the ring can twist more easily in one direction than another, resulting in an asymmetric ring. When the substituents are two identical phenyl groups as in compound II, the ring remains symmetrical. Since the packing of the bromide ions is asymmetrical in both compounds, this does not appear to have a strong influence on the ring conformation here. Examination of contact distances between bromide ion and atoms in the molecule fails to reveal any particularly short distances.

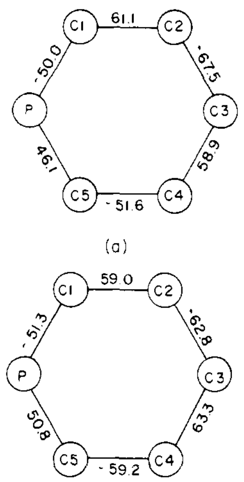


Figure 5. Torsional angles (deg) in the heterocyclic ring of (a) 1-benzyl-1-phenylphosphorinanium bromide (I) and (b) 1,1-diphenyl-4-methylphosphorinanium bromide (II).

Table VII. Deviations (Å) from Selected Least-Squares Mean Planes for I[a]

I[b]		II		III	
CB2	0.000	CP1	−0.006	C1	0.034
CB3	0.007	CP2	0.011	C2	−0.040
CB4	−0.004	CP3	−0.000	C4	0.038
CB5	0.002	CP4	−0.014	C5	−0.033
CB6	−0.006	CP5	0.017	P	(−0.765)
CB7	0.001	CP6	−0.007	C3	(0.687)

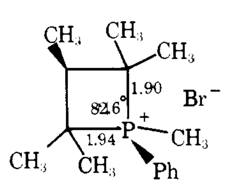
[a] Entries in parentheses are for atoms not included in the calculation of the plane. [b] Selected dihedral angles (deg) between planes indicated: I and II = 63.6, II and III = 100.5, III and (C1-P-C5) = 44.5, III and (C2-C3-C4) = 56.5, I and III = 82.4.

Table VIII. Deviations (Å) from Selected Least-Squares Mean Planes for II[a]

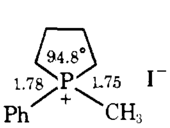
I[b]		II		III	
CP1	0.003	CP7	0.007	C1	−0.001
CP2	0.001	CP8	0.000	C2	0.001
CP3	−0.007	CP9	−0.007	C4	−0.001
CP4	0.008	CP10	0.008	C5	0.001
CP5	−0.004	CP11	−0.001	P	(0.813)
CP6	−0.002	CP12	−0.006	C3	(−0.707)
P	(0.048)	P	(0.016)		

[a] Entries in parentheses are for atoms not included in the calculation of the plane. [b] Selected dihedral angles (deg) between planes indicated: I and III = 34.6, II and III = 104.1, III and (C1-P-C5) = 47.3, III and (C2-C3-C4) = 55.1.

With regard to particular structural features of I and II of special importance in modeling the course of alkaline hydrolysis, a comparison of the internal ring angles at phosphorus with those in the related four-[19] and five-[20] membered cyclic phosphonium salts III and IV is instructive. It is evident that



III



IV

the four- and five-membered rings can more readily span apical-equatorial sites of a trigonal-bipyramidal transition state

Table IX. "Strainless" Parameters Involving the Phosphorus Atom

	l_0, Å	k_s, mdyn/Å
P-C[a]	1.750	3.11
C_{sp^2}-C_{sp^2}	1.388[b]	7.33
	θ_0, deg	k_θ, mdyn·Å/rad^2
P-C_{sp^3}-C_{sp^2}	110.2	0.38
P-C_{sp^2}-C_{sp^2}	120.0	0.97
P-C_{sp^3}-C_{sp^3}	110.5	0.38
P-C_{sp^3}-H	109.5	0.60

[a] All P-C bonds have the same parameters. [b] Included here since it is different from Allinger's programmed value in MMI in ref 21 and 22.

Table X. Calculated Energies (kcal/mol) for Conformers of 1-Benzyl-1-phenyl-4-methylphosphorinanium Bromide

	Ia[a]	Ib	IIa	IIb
stretch	3.49	3.40	3.37	3.49
bend	2.40	1.80	1.74	2.61
1,4 VDW	7.14	6.31	6.51	6.86
other VDW	18.46	19.23	18.75	19.01
1,3 VDW	24.48	24.91	24.56	25.00
torsion	0.02	0.02	0.02	0.04
total	31.52	30.77	30.39	32.01

[a] Roman numerals refer to numbering system used in Figure 6.

Table XI. Steps for Modeling the Inversion Pathway

steps	P-O l_0, Å	k_s, mdyn/Å	P-CB_{14} l_0, Å	k_s, mdyn/Å
1	3.50	0.000	1.75	3.110
2	3.00	0.184	1.75	3.110
3	2.50	0.400	1.90	1.900
4	2.10	0.921	2.10	1.095

postulated to form during the course of hydroxide ion attack than to span diequatorial sites. For I and II containing six-membered rings, the presence of an internal ring angle at phosphorus near 105° should make the retention and inversion routes more competitive as discussed in the Introduction.

As a further consideration the phenyl group in I is rotated about the P-C bond so that its hydrogens avoid steric interactions with the axial hydrogens of the heterocyclic ring. The dihedral angle between the plane of the phenyl group and the plane through atoms C_1, C_2, C_4, and C_5 is 100.5°; cf. Table VII. In this position the phenyl group would not offer steric hindrance to attack by hydroxide ion approaching opposite the benzyl group. All phenyl groups in both compounds are planar as shown in Tables VII and VIII.

Molecular Mechanics Study of the Base Decomposition of *cis*- and *trans*-1-Phenyl-1-benzyl-4-methylphosphorinanium Bromide. Force Field. As a means of investigating the product distribution of the *cis*- and *trans*-1-phenyl-1-benzyl-4-methylphosphorinanium compounds (entries 1 and 2 of Table II), these systems were studied by the molecular mechanics technique. A parameter set was developed to reproduce good starting structures for these isomers. Then a hydroxide ion was introduced into the calculations and allowed to approach the phosphorus atom along a reaction coordinate. The energies and geometries of the intermediate structures were examined. The X-ray coordinates obtained for 1-benzyl-1-phenylphosphorinanium bromide (I) were used as an initial coordinate set in the calculations for two reasons: to avoid false minima problems and to get a proper orientation of the phenyl and benzyl groups. The X-ray study gives a low-energy conformation for

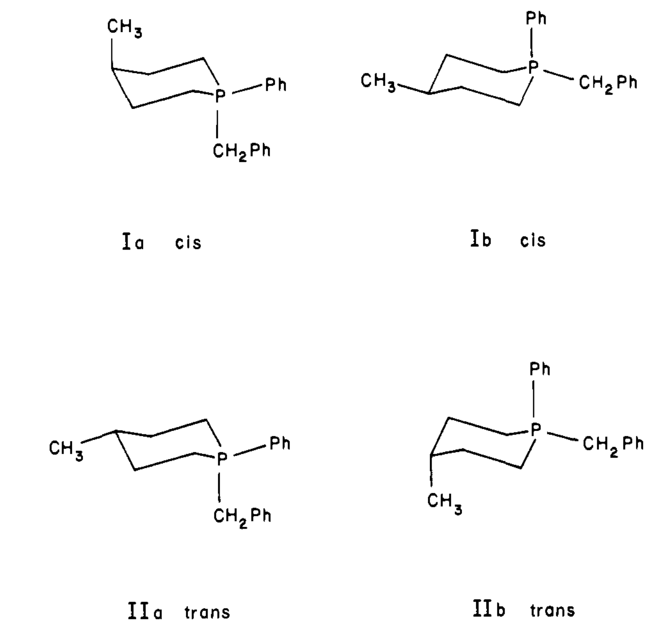


Figure 6. Conformations of *cis*- and *trans*-1-benzyl-1-phenyl-4-methylphosphorinanium bromide investigated via molecular mechanics.

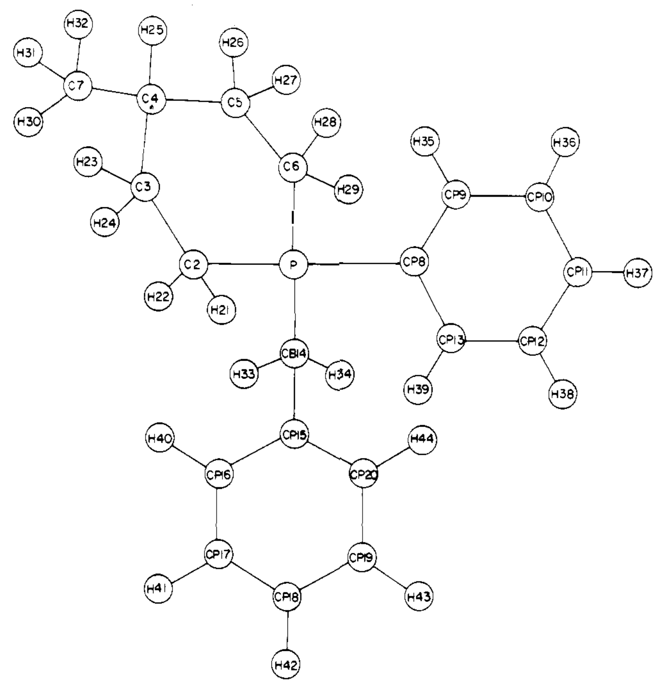


Figure 7. Numbering scheme used for the molecular mechanics calculations on 1-benzyl-1-phenyl-4-methylphosphorinanium bromide.

these rings, although rotation about the P–C bonds in solution may give other low-energy conformations.

A methyl group was added to the ring carbon atom at the 4 position and a parameter set was developed to reproduce the main features of the X-ray structure. This parameter set treats the phosphorus atom as a tetrahedral site with equivalent bond lengths and angles. We used the force field set up by Allinger in MMI,[21,22] and added bond length and angle parameters to account for the phosphorus atom. These are shown in Table IX.

One change from Allinger's parameter set was made here. This set assigns an l_0 of 1.334 Å to the C_{sp^2}–C_{sp^2} bonds. This caused some problems in the calculations, as the benzene ring carbons approached the heterocyclic ring too closely. The 1.388-Å length, found as an average value in the X-ray study, was used instead. The bending force constants about phosphorus were set equal to zero, so that in the study of the reaction coordinate the configuration about phosphorus may easily change from tetrahedral to trigonal bipyramid. To compensate for this lack of bending energy, 1,3 van der Waals interactions about phosphorus were included. We found[23] the inclusion of the latter interaction to be a desirable feature in the simulation of pentacoordinate phosphorus structures by molecular mechanics.

Two chair forms were investigated for each cis and trans isomer. These are shown in Figure 6. The X-ray structure shows the benzyl group in the equatorial position (with reference to cyclohexane nomenclature). This may not be the only conformation in solution. The other chair form, where the benzyl group is axial, may also be present. In these calculations the assumption was made that only two chair forms are present per isomer, any boat or twisted boat forms being unlikely.

After reproducing the X-ray structure as closely as possible, the parameter set was applied to calculating the geometries of the conformations in Figure 6. Their calculated energies are shown in Table X. The numbering system used for these and subsequent calculations is shown in Figure 7.

Hydrolysis Reaction Model. For modeling the inversion pathway, a hydroxide ion was introduced into the calculations and allowed to approach the tetrahedral face containing the C_2, C_6, and CP_8 atoms. In this way, attack was occurring directly opposite the benzyl group and the heterocyclic ring was forced to occupy diequatorial sites of a TP. Series of calculations were done for each isomer where the bond lengths of the entering and leaving groups were adjusted as in Table XI. As the bond lengths changed, the force constants were adjusted according to Badger's rule.[24] The bond lengths and force constants of the three P–C bonds, which become equatorial in the TP, remained at 1.75 Å and 3.11 mdyn/Å, respectively. The justification for lengthening the P–CB_{14} as the OH^- approaches is that this actually occurred in step 2 of the calculations. As OH^- approached P, the C_2, C_6, and CP_8 groups moved into a more planar arrangement about P. This resulted in increased 1,3 interactions between the CB_{14} atom and C_2, C_6, and CP_8, forcing the P–CB_{14} bond to lengthen as a means of decreasing the energy.

Step 4 was chosen to have equal bond lengths for P–O and P–C. All angles with phosphorus as the central atom have k_θ = 0.0 mydn·Å/rad^2, except for the CB_{14}–P–O angle with k_θ = 1.0 mdyn·Å/rad^2.[25] If no force constant is put on the latter angle, the OH^- ion may attack the phosphorus at a wide variety of angles (while still attacking opposite the benzyl group) and it would be difficult to make a comparison between conformers. Also, during the formation of a preferred trigonal-bipyramidal transition state, an attacking nucleophile might be expected to be increasingly oriented in an apical position as bonding electron density builds in this direction.

Steric energies are computed for the various steps along the reaction coordinate and compared in Table XII with ground-state steric energies. A relative transition-state energy is also given for each conformer which shows a high energy, 5.8 kcal/mol, for IIb (cf. Figure 6) compared to much lower values for reaction coordinates of the other conformers. The small differences between transition-state energies for Ia, Ib, and IIa are not considered especially significant. Hence, even if it is assumed that each of the cis and trans conformers is present in solution in equal amounts (although the X-ray structure of I favors Ib and IIb), inversion seems less likely for competitive OH^- attack on the trans isomer system compared to the cis.

Figure 8 is an ORTEP plot of conformer IIb at step 2. A steric interaction between the benzyl and axial ring methyl groups is evident. The benzyl group tries to move to lessen this interaction, but cannot move too far, owing to the OH^- constrained to attack directly opposite it and the interaction between the

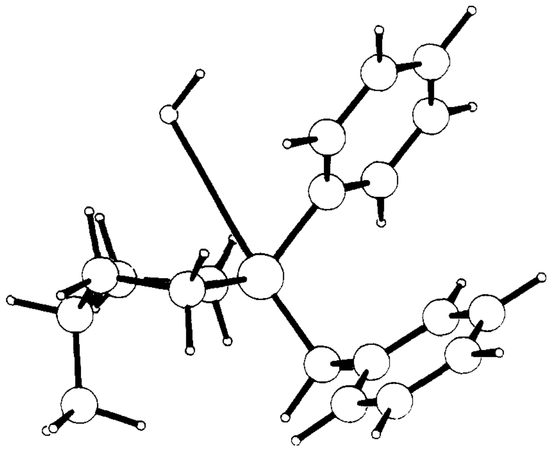


Figure 8. ORTEP plot of isomer IIb at step 2 of the reaction coordinate. Restriction used: ∠O-P-CB_{14} = 180°, k_θ = 1.0 mdyn·Å/rad^2.

benzyl and phenyl groups. Here the heterocyclic ring is approaching a half-chair form. The phosphorus atom is moving into the plane of the C_2, C_3, C_5, and C_6 atoms. The analogous step in the reaction coordinate for conformer Ib shows the ring in a twisted boat form and the ring methyl group not interfering with the benzyl group.

The results of the present calculation appear satisfactory in explaining why less inversion is observed for the trans isomer (Table II). However, additional insight might be obtained by investigating the energetics associated with the reaction coordinate for the competing retention pathway. This study would allow us to also comparatively evaluate overall reaction kinetics of different members. We speculate that the reduction in inversion (to 34%) observed[6b] for entry 3 of Table II (containing a ring *tert*-butyl group cis to the phenyl group) compared to the inversion (52%) for the corresponding ring methyl derivative (entry 1) probably is due to steric hindrance to in-line attack by OH^- in the conformer of the type Ia of Figure 6.

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Supplementary Material Available: A compilation of observed and calculated structure factor amplitudes, thermal parameters, and refined hydrogen atom positions for 1-benzyl-1-phenylphosphorinanium bromide (I) and 1,1-diphenyl-4-methylphosphorinanium bromide (II) (28 pages). Ordering information is given on any current masthead page.

Table XII. Reaction Coordinate Steric Energies (kcal/mol)[a]

	steric energies			
	Ia	Ib	IIa	IIb
ground state[b]	31.5	30.8	30.4	32.0
step 1[c]	31.1	30.5	29.8	31.5
step 2	33.7	33.4	31.8	37.8
step 3	33.2	32.8	31.3	35.4
step 4	33.0	32.8	31.3	33.5
Δ[d]	2.2	2.6	1.4	5.8

[a] Restriction used: ∠O-P-CB_{14} = 180°, k_θ = 1.0 mdyn·Å/rad^2. [b] See Table X for ground-state descriptions. [c] See Table XI for a definition of steps in the reaction coordinate. [d] Relative transition-state energy.

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