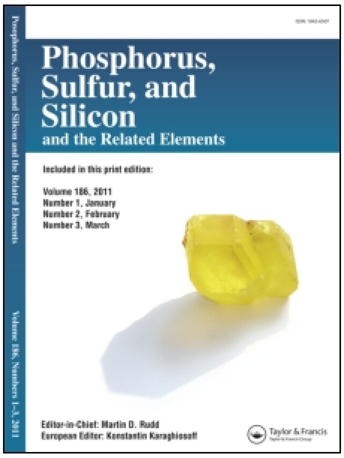

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OXYPHOSPHORANE ANIONS AS NUCLEOPHILES IN INTRAMOLECULAR DISPLACEMENT REACTIONS

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OXYPHOSPHORANE ANIONS AS NUCLEOPHILES IN INTRAMOLECULAR DISPLACEMENT REACTIONS

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Dedicated to Professor Reinhard Schmutzler on the occasion of his 60th birthday

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The present paper reports a kinetic study of alkaline decomposition of four bromoalkytriphenyl phosphonium bromides with the bromo-substituent in 3-, 4-, 5, and 6-positions, respectively (hereafter designated 3Br-P, 4Br-P, 5Br-P, and 6Br-P), together with the alkaline decomposition of 1,1,4,4-tetrabenzyl-1,4-diphosphoniocyclohexane dibromide (designated 2P). The very high rates of decomposition of 3Br-P and 2P are in accordance with an easy formation of five-membered oxaphospholane ring intermediates through participation of oxyphosphorane anions in intramolecular displacement reactions, with carbon in 3Br-P, and with phosphorus in the neighbouring phosphonium cation of 2P.

Key words: Oxyphosphorane anions, bromoalkyltriphenyl phosphonium bromides, 1,1,4,4-tetrabenzyl-1,4-diphosphoniocyclohexane dibromides.

The third order reaction kinetics of the alkaline decomposition of organic phosphonium compounds has led to the postulate that the reaction takes place through a hydroxyphosphorane, which is ionized to the corresponding oxyphosphorane anion, before decomposition to phosphine oxide and carbanion (Figure 1)[1–4].

The stability of hydroxyphosphoranes, and especially their anions, is too low to permit direct detection. Corresponding methoxyphosphoranes have, however, been detected by NMR,[5] and the cyclic oxyphosphorane: 2,2,2-triphenyl-1,2-oxaphospholane has been prepared in good yield by treating 3-hydroxypropyl-triphenyl phosphonium iodide with sodium hydride in tetrahydrofuran.[6] According to the bipyramidal configuration of pentacovalent phosphorus compounds, and the preferred placement of the most negative substituents in axial positions, the hydroxyphosphorane intermediate ought to have the hydroxy group in axial position.[7] But since the P—O and P—C bonds are much stronger in equatorial position, the hydroxyphosphorane is supposed to undergo pseudorotation, placing the hydroxy

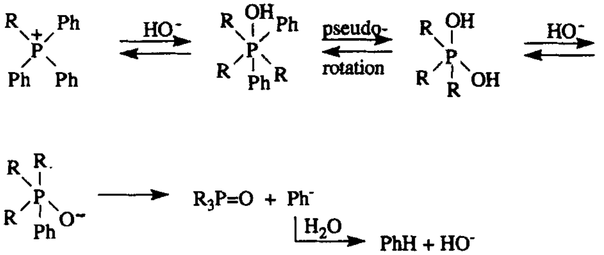


FIGURE 1

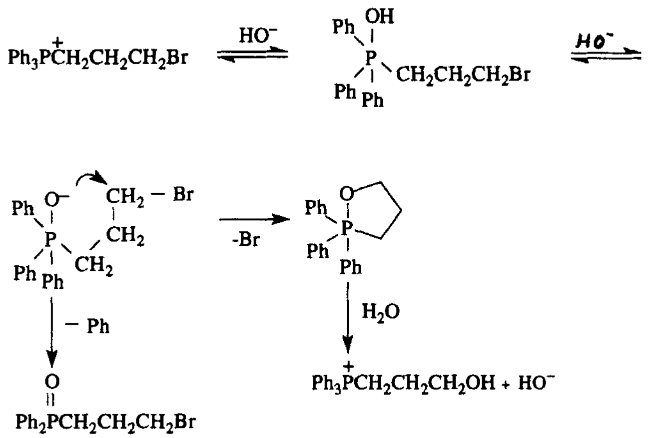


FIGURE 2

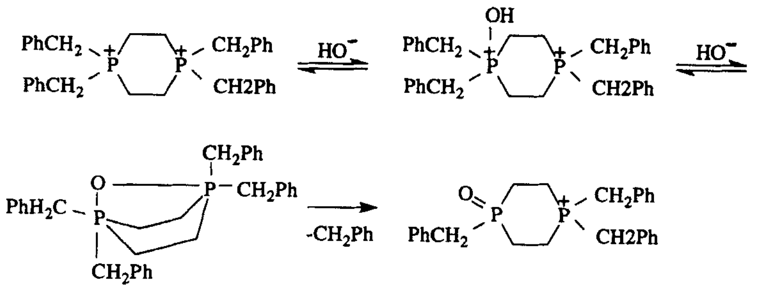


FIGURE 3

group in equatorial position, and the leaving group in axial position, before deprotonation and splitting of the P—C bond take place (Figure 1).

Although the oxyphosphorane anion cannot be detected directly, its presence might be proved indirectly by intramolecular reaction with a favourable placed electrophilic center in the same molecule. The present paper reports the alkaline decomposition of four bromoalkyltriphenyl phosphonium salts, containing the bromosubstituent in 3-, 4-, 5-, and 6-position, respectively, designated 3Br-P, 4Br-P, 5Br-P, and 6Br-P. If the oxyphosphorane anion displaces the bromide ion in intramolecular substitution, each reaction should proceed through correspondingly unstable 5-, 6-, 7-, and 8-membered oxyphosphorane ring intermediates. The reaction scheme is outlined for 3Br-P in Figure 2.

On the other hand, an intramolecular displacement reaction of the oxyphosphorane anion of 1,1,4,4-tetrabenzyl-1,4-diphosphoniocyclohexane during its alkaline decomposition ought to take place with the P-atom of the second phosphonium group, forming a pentacovalent five-membered ring intermediate where both P-atoms can obtain axial placement of the joint oxygen atom (Figure 3).

EXPERIMENTAL

The four bromoalkyltriphenyl phosphonium salts: 3-bromopropyl-, 4-bromobutyl-, 5-bromopentyl-, and 6-bromohexyltriphenyl phosphonium bromides, were obtained from the reaction between triphenyl phosphine and the respective primary alkyl dibromides in benzene solution. After several recrystallizations from ethanol/ether and/or chloroform/ether, constant melting points and satisfactory bromide analysis of the salts were obtained.[8]

1,1,4,4-tetrabenzyl-1,4-diphosphoniocyclohexane dibromide (2P) was made in the following way: Tribenzylphosphine reacts with 1,2-dibromethane forming bis-1,2-tribenzylphosphonium ethane dibromide, which was reduced with $LiAlH_4$ to bis-1,2-dibenzylphosphine ethane, and the latter compound treated with 1 mol 1,2-dibromethane, producing the cyclic diphosphonium compound 2P in good yield. 2P was recrystallized several times from methanol/water until constant melting point, 290°C.[9] Ionic bromide analysis as well as the NMR spectrum was in accordance with the anticipated structure of 2P.

Rate measurements: The rates of the alkaline decomposition of the phosphonium salts were measured at different temperatures in 50% DMSO/water, using equivalent amounts of substrate and sodium hydroxide (Table I).

The very rapid alkaline decomposition of 2P was followed by potentiometric titration at constant pH between 10 and 11. The exact HO^- concentration at the fixed pH chosen in each experiment was determined separately.

INTRAMOLECULAR REACTION OF: $\gt P-O^-$ WITH $-\overset{|}{\underset{|}{C}}-Br$

The alkaline decomposition of the four bromoalkyltriphenyl phosphonium salts can take place by three routes: a) Intermolecular displacement of the bromo group

TABLE I

Third order rate constants of alkaline decomposition of $Br(CH_2)_nP^+Ph_3$ in 50% $DMSO/H_2O$

Compound $Br(CH_2)_nP^+Ph_3$	Temperatur °K	Rate constant k $l^2 M^{-2} s^{-1}$	Arrhenius kcal/M	Arrhenius log A
n=3	298.15	37.2	23 ±1	19 ±1
	303.05	66.1		
	307.00	150		
	312.85	229		
	323.15*	977		
n=4	337.85	4.07	20 ±2	13 ±2
	343.35	6.76		
	346.95	9.12		
	349.95	11.2		
	323.15*	1.10		
n=5	326.95	17.4	21 ±3	15 ±2
	331.45	27.5		
	336.40	50.1		
	341.35	67.6		
	323.15*	12.0		
n=6	316.35	0.72	23 ±4	15 ±4
	318.85	1.10		
	321.15	1.25		
	323.15*	1.74		
$CH_3P^+Ph_3$	323.15**		31	21

* Estimated rate constants. ** Data from earlier study.[3]

by a hydroxyl ion according to second order kinetics. b) Intramolecular displacement of the bromo group by the oxyphosphorane anion, resulting in third order kinetics, first order in phosphonium and second order in hydroxyl ions. 3) Direct decomposition of the phosphorane anion to bromoalkyldiphenylphosphine oxide and benzene, also according to third order kinetics.

Of the four phosphonium salts studied, the 3Br-P compound decomposes quantitatively to the corresponding 3-hydroxypropyltriphenyl phosphonium ion, following third order kinetics, and indicating that the reaction takes place by intramolecular substitution with the phosphorane anion (Figure 2). The half life of decomposition of an equimolecular mixture of phosphonium compound and sodium hydroxide (0.006 mol/l) is 4800 times faster than the half life of decomposition of an equimolecular mixture of 1-bromopropane and sodium hydroxide of the same concentration. Thus, the very high rate, as well as the change of kinetics, are in accordance with intramolecular displacement of bromide ions by oxyphosphorane anions.

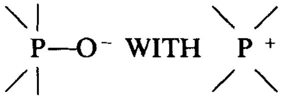
The products of the alkaline decompositions of the other bromoalkyl phosphonium ions, 4Br-P, 5Br-P, and 6Br-P, are bromide ions and the corresponding hydroxyalkyltriphenyl phosphonium ions, but small amounts of bromoalkyl diphenylphosphine oxides and benzene are also formed, indicating a slight competition from direct decomposition of phosphorane anions. Since the kinetics of the decomposition deviate somewhat from third order rate dependence, it is likely that a second order intermolecular displacement reaction by hydroxyl ions might also compete slightly with the intramolecular substitution route.

The half life of the hydrolysis of the four phosphonium salts relative to 3Br-P are: 3Br-P: 1, 4Br-P: 260, 5Br-P: 40, 6Br-P: 315, 1-bromopropane: 4800. The much shorter half life of the 3Br-P compound, reveals the strong preference of formation of the oxaphospholane intermediate containing a five-membered ring. The results are in accordance with earlier observation that phosphonium salts where phosphorus is part of a five-membered ring, hydrolysis 10^3 times faster than similar compounds with bigger rings.[10]

Regarding the details of the intramolecular substitution, the question arises whether the proton is split off from the OH group in axial or equatorial position (after pseudo-rotation) (cfr. Figure 1). It is well known that substituents in pentacovalent phosphorus compounds are more strongly bounded in equatorial position than in axial position, and equatorial deprotonation should therefore be easier. The transition state during intramolecular substitution would then have the bromoalkyl group in either equatorial or axial position. But since oxygen is the most electronegative atom, oxygen will always have axial placement in the cyclic intermediate, 2,2,2-triphenyl-1,2-oxaphospholane which is formed. Therefore, it seems more likely to assume a concerted reaction, where solvent HO^- is attacking the hydroxyl group in its axial position when its oxygen is favourably placed in relation to the 3-carbon atom of the 3-bromopropyl group, resulting in simultaneous rupture of the O—H and C—Br bonds (Figure 2).

In Table I are collected the rate data of the alkaline hydrolysis of the four bromoalkyltriphenyl phosphonium compounds, measured in 50% DMSO/water, together with their calculated activation parameters. For comparison, the activation parameters of the alkaline hydrolysis of the methyltriphenyl phosphonium, where decomposition of the intermediate oxyphosphorane anion to methyldiphenylphosphine oxide and benzene takes place, are also included. The activation energy of the latter is around 10 kcal/mol higher than the activation energy of the four bromoalkylphosphonium compounds in Table I, clearly indicating different reaction mechanisms. The same conclusion can also be arrived at from the higher log A factor of the direct decomposition of the oxyphosphorane anion in comparison with its intramolecular C—Br displacement reaction. The former is a monomolecular reaction, the latter reaction is dependent upon encounter of O^- with the C—Br group which is free to move, resulting in reduced encounter frequency.

The extraordinary high rate of the alkaline decomposition of the 3Br-P compound in comparison with the 4-, 5-, and 6Br-P compounds, is characterized by an unusual high log A value, 4–6 units higher of the former, pointing to a much more favourable geometry of the five-membered oxaphospholane transition state. The 10 times higher rate of 5Br-P than 4Br-P shows that a seven-membered transition state might be preferred to a six-membered one. A similar observation regarding ring preference in phosphorus compounds was noticed for the intramolecular hydrogen bonding in hydroxyalkyl diphenylphosphine oxides, where the H-bond in the seven-membered ring is considerably stronger than in the six-membered ring.[10]



INTRAMOLECULAR REACTION OF: P—O$^-$ WITH P$^+$

The soft electrophilic carbon in C—Br is not the best matching for the hard oxygen nucleophile of the phosphorane anion. However, the P-atom in phosphonium compounds is a hard, strongly electrophilic center. Therefore, if a second phosphonium group is favourably placed in relation to the anion of the oxyphosphorane, and especially if a five-membered ring containing the P—O—P bond is formed, very high rate of forming the unstable reaction intermediate ought to be expected. The tetrabenzyl substituted diphosphonium compound 2P (Figure 3) contains a cyclohexane ring where the C-atoms in 1- and 4-positions are replaced with phosphorus. The intramolecular reaction of the oxyanion with the second P-atom will give rise to a double phosphorane intermediate where the joint oxygen atom occupies axial positions in two five-membered rings.

In the alkaline decomposition of 0.0005 M 2-P with 0.001 M NaOH, enough base to split off two benzyl groups, the half life of reaction was approximately 5 minutes. The consumption of alkali shows that the reaction stops after one benzyl group is removed (Figure 4). When a second benzyl group is going to be split off, from the other phosphonium group, its neighbour P-atom belongs to a phosphine oxide in which the P-atom has low electrophilicity in comparison to P in phosphonium cations, preventing intramolecular P—O—P bond formation. The decomposition will therefore follow the normal slow route: the direct decomposition of the oxyphosphorane anion.

The rate of the decomposition of the first benzyl group in 2-P was determined by potentiometric titration at constant pH. In Table II are collected rate data at three temperatures measured at pH 10,1 in 90% methanol/water, together with

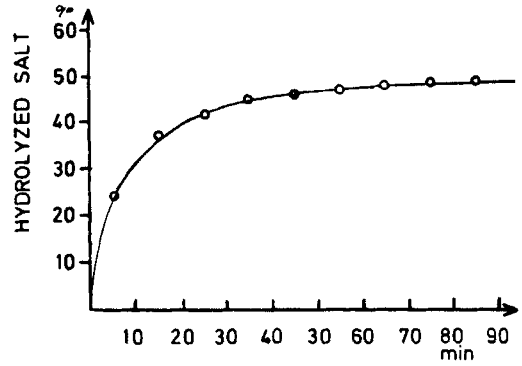


FIGURE 4

TABLE II

Rate constants and activation parameters for the alkaline decomposition of 1,1,4,4-tetrabenzyl-1,4-diphosphoniocyclohexane dibromide pH 10.1 in 90% methanol/water

Temperature ^{0}C	Rate constant k (l $M^{-2}s^{-1}$)	Arrhenius kcal/M	Arrhenius logA
40.00	384		
45.00	974	39±2	29±2
50.00	2683		

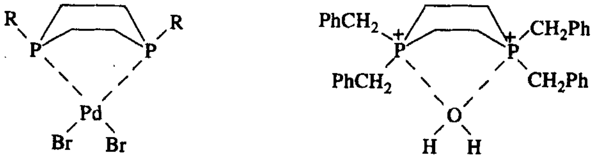


FIGURE 5

the calculated activation parameters. The unusual high activation energy, 39 kcal/mol is compensated by a correspondingly high log A factor, 29, indicating extremely high probability of forming the double five-membered phospholane intermediate. The observation that 2-P has 1 mol of crystal water, which persists even at heating in vacuo at 100°C for 2 hours, suggest very strong coordination of the water molecule. For comparison, the configuration of complexes of palladium with corresponding six-membered 1,4-diphosphophosphoniocyclohexane derivatives shows that both phosphorus atoms are coordinated to the same palladium atom, resulting in boat configuration of the cyclohexane ring.[9] If a similar structure exists for the 2-P hydrate, the easy formation of its oxaphospholane intermediate in alkaline solution can be understood (Figure 5).

Earlier report[11] of rapid isomerisation during alkaline decomposition of similar cyclic diphosphonium salts, cis- or trans-1,4-dibenzyl-1,4-diphenyl-1,4-diphosphoniocyclohexane dibromide, into a mixture of corresponding cis and trans diphosphine dioxides, can also be explained as due to O—P—O ring closure since pseudorotation of neutral oxyphosphoranes, resulting in isomerisation, are known to be fast processes.

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