diphenylthiophosphinic chloride. After heating under reflux in an argon atmosphere for 18 hr., the solvent was removed at reduced pressure, yielding a semisolid. After washing with dilute ammonium hydroxide and digestion with isopropyl alcohol, 8.0 g. (0.027 mole, 91% yield) of triphenylphosphine sulfide, m.p. 158–160°, was obtained. Acidification of the basic extract with concentrated hydrochloric acid yielded 6.5 g. of impure diphenylphosphonic acid, m.p. 185–190°, as confirmed by the infrared spectrum of the solid.

Acknowledgments.—We wish to thank Messrs. Karl Sterner and William Birch for the elemental analyses and Mrs. Nancy Naumann for the infrared spectra.

Organometallic Azides. II. Preparation and Reactions of Phenylphosphonic Mono- and Diazides[1]

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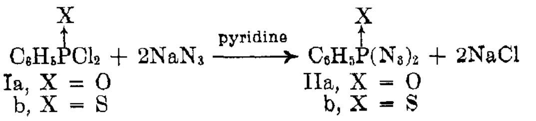
The synthesis and reactions of thermally unstable phenylphosphonic and phenylthiophosphonic diazide are described. These diazides react stepwise with triphenylphosphine to yield intermediate azidophosphoranes, $C_6H_5\underset{N_3}{\underset{|}{P}}(X)N{=}P(C_6H_5)_3$, which further react to yield bisphosphoranes, $C_6H_5P(X)[N{=}P(C_6H_5)_3]_2$. The chemistry of several mixed phosphonic azides, $C_6H_5\underset{Z}{\underset{|}{P}}(O)N_3$ [Z = Cl, $N(CH_3)_2$] is also described.

The syntheses of the stable diarylphosphinic azides from phosphinic chlorides and sodium azide in pyridine and their reaction to yield N-(diarylphosphinyl)-iminophosphoranes[2] as well as the addition of bromine to the N-(diarylphosphinyl)iminophosphoranes[3] have been recently described.

As a result of the thermal and chemical stability of N-diphenylphosphinyl-P,P,P-triphenyliminophosphorane,[2] it was of interest to synthesize and evaluate polyphosphorane polymers for use as thermally stable materials. One of the necessary intermediates required for the preparation of polyphosphoranes are aromatic phosphonic diazides such as II. Phenylphosphonic and phenylthiophosphonic dichlorides (Ia and b, respectively) were found to react smoothly with sodium azide in pyridine to yield the diazides IIa and b.

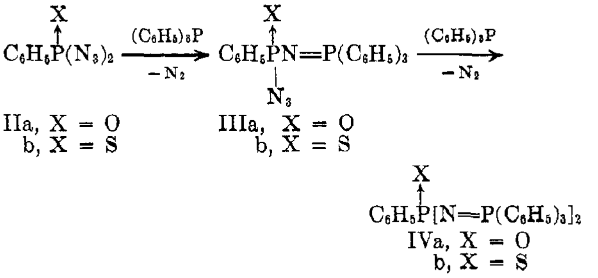

$$C_6H_5\overset{\overset{X}{\uparrow}}{P}Cl_2 + 2NaN_3 \xrightarrow{\text{pyridine}} C_6H_5\overset{\overset{X}{\uparrow}}{P}(N_3)_2 + 2NaCl \qquad (1)$$

Ia, X = O
b, X = S

IIa, X = O
b, X = S

In marked contrast to the thermal and shock stability of the previously prepared diarylphosphinic azides,[2] $Ar_2P(O)N_3$, IIa was found to be extremely shock sensitive and it "verpufft" when placed in a bunsen flame. Furthermore, during the attempted distillation of the thiophosphonic diazide IIb at 0.1 mm., the sample detonated, completely demolishing the distillation apparatus. Pyridine solutions of these phosphonic diazides did not show any shock or thermal sensitivity. However, as a matter of safe practice, all solutions of these and other azides were frequently tested for shock sensitivity.

In preparing the bisphosphoranes IVa and b which were to serve as reference compounds and prototypes for the polyphosphoranes, it was discovered that phenylphosphonic diazide (IIa) in pyridine solution reacted in a clearly defined stepwise manner with 2 equiv. of triphenylphosphine (eq. 2). The first mole of triphenylphosphine at ambient temperature reacted exothermally and then the reaction essentially stopped even in the presence of a second mole of triphenylphosphine. A strong azide absorption was still present at 2138 cm.$^{-1}$ at this halfway point. The nitrogen evolution to this point was 51.35% of the total nitrogen or 102.7% of the nitrogen expected by reaction of only one of the azide groups. The azide function of IIIa subsequently reacted with triphenylphosphine only slowly at reflux in pyridine. The resulting bisphosphorane IVa was isolated as a powder which was difficult to obtain in a crystalline form. Like the N-(diarylphosphinyl)-P,P,P-triphenyliminophosphoranes,[2] IVa was found also to be stable toward attack by aqueous acid and base.


$$C_6H_5\overset{\overset{X}{\uparrow}}{P}(N_3)_2 \xrightarrow[-N_2]{(C_6H_5)_3P} C_6H_5\overset{\overset{X}{\uparrow}}{\underset{N_3}{\underset{|}{P}}}N{=}P(C_6H_5)_3 \xrightarrow[-N_2]{(C_6H_5)_3P} C_6H_5\overset{\overset{X}{\uparrow}}{P}[N{=}P(C_6H_5)_3]_2 \qquad (2)$$

IIa, X = O
b, X = S

IIIa, X = O
b, X = S

IVa, X = O
b, X = S

Similarly, the reaction of phenylphosphonyl diazide (IIb) with triphenylphosphine was found to be stepwise. Isolation of the intermediate azidophosphorane IIIb in a pure solid state was not accomplished although there was not any evidence of hydrolysis products (by infrared examination) in the tacky IIIb which was recovered after removal of the pyridine. The azidophosphorane IIIb was, however, characterized by conversion to its methyl ester V and to the bisphosphorane

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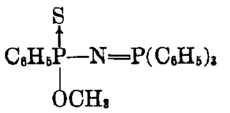
[1] (a) This investigation was supported by the Materials Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio, under Contract AF 33(657)-11129. (b) Presented before the Division of Organic Chemistry at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964.

[2] (a) R. A. Baldwin and R. M. Washburn, *J. Am. Chem. Soc.*, **83**, 4466 (1961); (b) R. A. Baldwin and R. M. Washburn, *J. Org. Chem.*, **30**, 3860 (1965).

[3] R. A. Baldwin and R. M. Washburn, *ibid.*, **30**, 2093 (1965).

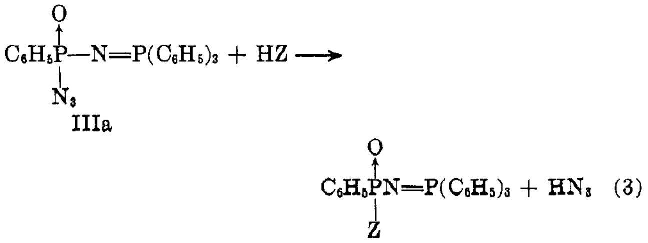


$$\mathrm{C_6H_5\overset{S}{\overset{\uparrow}{P}}(OCH_3){-}N{=}P(C_6H_5)_3}$$

V

IVb which was more readily separated and purified than IVa. The bisphosphorane IVb was also found to be stable toward dilute aqueous sodium hydroxide and sulfuric acid at ambient temperature.

The azidophosphorane IIIa is an interesting compound. In contrast to the hydrolytic sensitivity of IIa and b, as well as the phosphinic azides,[2] IIIa could be precipitated in high purity from the pyridine reaction solution by means of water and only reacted sluggishly with methanol in pyridine solution to give the corresponding methoxyphosphorane VIa. In addition, IIIa was recovered from aqueous sodium hydroxide after 8 hr. on the steam bath without any evidence for conversion to the acid VIb. Hydrolysis was effected by means of refluxing alcoholic sodium hydroxide and a low yield of the acid phosphorane VIb was isolated (however, see below for the facile synthesis of VIb). Further characterization of the azidophosphorane IIIa gave the anilide VIc and the N,N-diethylaminophosphorane VId. Both reactions were sluggish and the yields were poor (eq. 3). The azidophosphorane was also unaffected on heating to 200°. Continued heating to 245° for 5 hr. then resulted in the loss of the characteristic azide absorption. Unfortunately, the initial analyses for the product do not support a simple cyclic thermolysis product. Other studies of this thermolysis are underway. This unique combination of chemical and thermal stability exhibited by IIIa might seem to suggest that the azide group might no longer be present as such but perhaps be in a heterocyclic form. However, this does not seem to be the case as the infrared spectrum of IIIa still contained a typical strong azide absorption at 2140 cm.$^{-1}$.

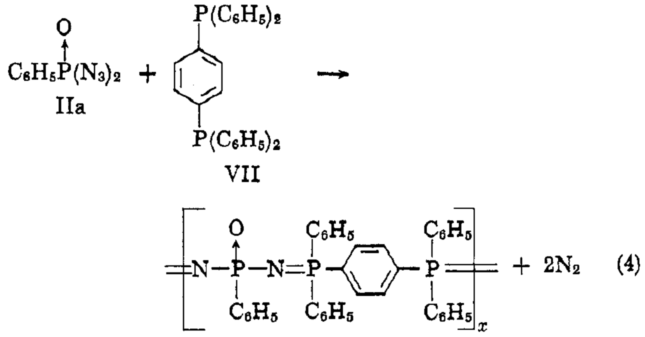


$$\mathrm{C_6H_5\overset{O}{\overset{\uparrow}{P}}(N_3){-}N{=}P(C_6H_5)_3 + HZ \longrightarrow C_6H_5\overset{O}{\overset{\uparrow}{P}}(Z)N{=}P(C_6H_5)_3 + HN_3} \quad (3)$$

IIIa

VIa, Z = OCH_3
b, Z = OH
c, Z = NHC_6H_5
d, Z = $N(C_2H_5)_2$

The initial synthesis of a polyphosphorane polymer was carried out by adding a solution of phenylphosphonic diazide (IIa) to a pyridine slurry of 1,4-bis-(diphenylphosphino)benzene (VII) (eq. 4). This reaction also proceeded in a stepwise manner which suggested that isolation of the intermediate azidophosphorane IXa might be possible. The reaction product VIII was soluble in pyridine and was isolated as a light tan powder which had a wide softening range (100–160°). After drying on the high vacuum line at 100–140° for several hours, the powder appeared to soften at about 160–170°. A molecular weight determination on a benzene-soluble fraction of this crude polymer gave a value of approximately 2300 which would represent a degree of polymerization of about 4. Infrared examination of the crude polyphosphorane showed the presence of a weak azide absorption at 2138 cm.$^{-1}$. This would seem to imply that the bis tertiary phosphine VII was impure or that the stoichiometry was not 1:1.



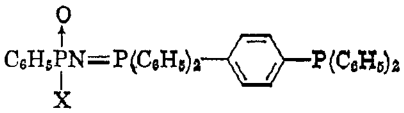
$$\mathrm{C_6H_5\overset{O}{\overset{\uparrow}{P}}(N_3)_2 + 1,4\text{-}[(C_6H_5)_2P]_2C_6H_4 \longrightarrow \left[{=}N{-}\overset{O}{\overset{\uparrow}{P}}(C_6H_5){-}N{=}P(C_6H_5)_2{-}C_6H_4{-}P(C_6H_5)_2{=}\right]_x + 2N_2} \quad (4)$$

IIa

VII

VIII

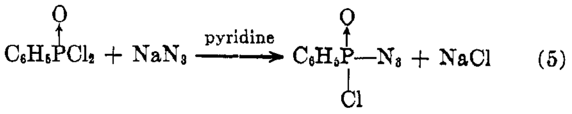
The stepwise nature of the reaction of phosphonic diazides and tertiary phosphines as well as the chemical stability of the azidophosphorane IIIa suggested that it would be of interest to attempt the isolation of the polymer intermediate azidophosphorane IXa. Isolation and purification of IXa would then ensure a 1:1 stoichiometry necessary in the subsequent conversion to the polyphosphorane VIII. Unfortunately, during the attempted isolation of IXa polymerization to the polyphosphorane took place.



$$\mathrm{C_6H_5\overset{O}{\overset{\uparrow}{P}}(X)N{=}P(C_6H_5)_2{-}C_6H_4{-}P(C_6H_5)_2}$$

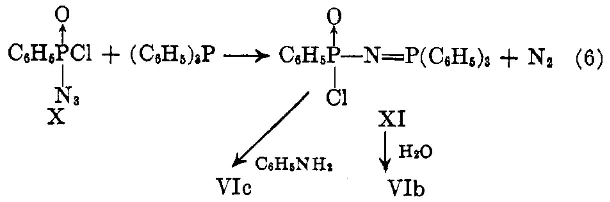
IXa, X = N_3
b, X = Cl
c, X = $N(CH_3)_2$

An alternative to the isolation of IXa would be the preparation and isolation of the corresponding chlorophosphorane IXb. This compound would have the advantage of not undergoing polymerization during its purification. To test this approach, the following investigative reactions were carried out (eq. 5 and 6).



$$\mathrm{C_6H_5\overset{O}{\overset{\uparrow}{P}}Cl_2 + NaN_3 \xrightarrow{\text{pyridine}} C_6H_5\overset{O}{\overset{\uparrow}{P}}(Cl){-}N_3 + NaCl} \quad (5)$$

Ia X



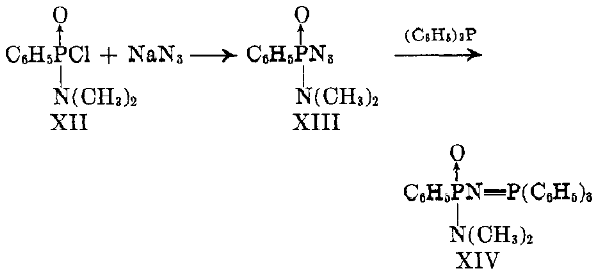
$$\mathrm{C_6H_5\overset{O}{\overset{\uparrow}{P}}(N_3)Cl + (C_6H_5)_3P \longrightarrow C_6H_5\overset{O}{\overset{\uparrow}{P}}(Cl){-}N{=}P(C_6H_5)_3 + N_2} \quad (6)$$

X XI

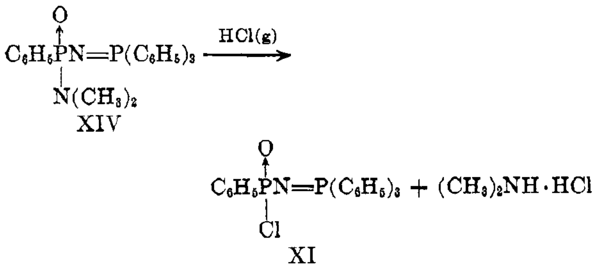
$$\mathrm{XI \xrightarrow{C_6H_5NH_2} VIc \qquad XI \xrightarrow{H_2O} VIb}$$

Phenylphosphonic dichloride in pyridine was treated with only 1 equiv. of sodium azide (eq. 5) to yield the phosphonic azidochloride X. Attempted purification by distillation at reduced pressure resulted in the isolation of a liquid–solid mixture which was not shock sensitive although it burned vigorously when placed in a bunsen flame. When X was treated with 1 equiv. of triphenylphosphine at ambient temperature, there was an exothermic reaction which resulted in a quantitative liberation of nitrogen (eq. 6).[4] However, in contrast to the marked hydrolytic stability of the azidophosphorane IIIa, the chlorophosphorane XI was quantitatively hydrolyzed to the acid VIb when the pyridine reaction mixture was poured into water for isolation. Reaction of XI with aniline readily yielded the anilide VIc in contrast to the sluggish reaction of the azidophosphorane IIIa and aniline (see above).

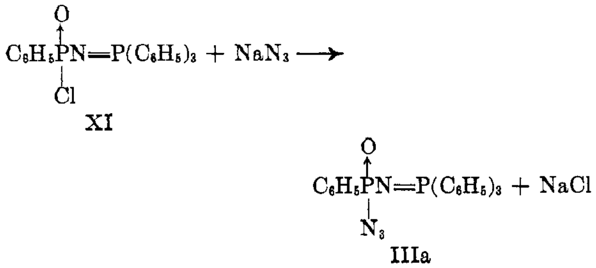
Since it was not possible to isolate and purify the polymer intermediate IXa and it was anticipated that the corresponding chloro compound IXb would be hydrolytically sensitive, it was felt that the dimethylamino derivative IXc could be prepared, purified, and perhaps reconverted to IXa. To evaluate this approach, the following sequence of reactions was studied since several of the intermediates would be known compounds from previous studies (eq. 7–9).



$$\underset{\text{XII}}{C_6H_5\overset{\overset{O}{\uparrow}}{\underset{N(CH_3)_2}{P}}Cl} + NaN_3 \longrightarrow \underset{\text{XIII}}{C_6H_5\overset{\overset{O}{\uparrow}}{\underset{N(CH_3)_2}{P}}N_3} \xrightarrow{(C_6H_5)_3P} \underset{\text{XIV}}{C_6H_5\overset{\overset{O}{\uparrow}}{\underset{N(CH_3)_2}{P}}N{=}P(C_6H_5)_3} \quad (7)$$



$$\underset{\text{XIV}}{C_6H_5\overset{\overset{O}{\uparrow}}{\underset{N(CH_3)_2}{P}}N{=}P(C_6H_5)_3} \xrightarrow{HCl(g)} \underset{\text{XI}}{C_6H_5\overset{\overset{O}{\uparrow}}{\underset{Cl}{P}}N{=}P(C_6H_5)_3} + (CH_3)_2NH\cdot HCl \quad (8)$$



$$\underset{\text{XI}}{C_6H_5\overset{\overset{O}{\uparrow}}{\underset{Cl}{P}}N{=}P(C_6H_5)_3} + NaN_3 \longrightarrow \underset{\text{IIIa}}{C_6H_5\overset{\overset{O}{\uparrow}}{\underset{N_3}{P}}N{=}P(C_6H_5)_3} + NaCl \quad (9)$$

Phenyl-N,N-dimethylaminophosphonic chloride (XII) similarly reacted at ambient temperature with sodium azide to give the amino azide XIII which was readily purified and which was not shock sensitive. The reaction of the amino azide XIII with triphenylphosphine was slow at ambient temperature in contrast to the exothermic reaction of triphenylphosphine under similar conditions with most of the other phosphonic azides prepared in this work. Only about 70% of the nitrogen was evolved after 8 hr. at ambient temperature and it was necessary to reflux the mixture briefly to complete the reaction. The evolution of nitrogen was then quantitative and the azide absorption at 2155 cm.$^{-1}$ had disappeared.

It was next demonstrated that the chlorophosphorane XI could be readily converted into the azidophosphorane IIIa in an over-all yield from phenylphosphonic dichloride of 98%. Thus, if XI could be obtained from the aminophosphorane XIV, then this approach would provide access to the polymer intermediate IXa. However, the cleavage of the aminophosphorane XIV by means of anhydrous chloride, as shown in eq. 8, failed to yield any of the desired chlorophosphorane XI under mild reaction conditions. Evidence for the unsuccessful cleavage was the failure to isolate any of the acid phosphorane VIb which would readily form on the hydrolysis of XI. This stability of the aminophosphorane to the attempted cleavage by hydrogen chloride appears to rule out this approach (eq. 7–9) for obtaining pure polymer intermediate IXa. However, under more forcing conditions, *i.e.*, sealed tube, it may be possible to carry out this conversion. The hydrolytic stability of XIV was also demonstrated during the attempted aqueous alcoholic hydrogen chloride hydrolysis which resulted in a yield of only slightly more than 50% of the acid phosphorane VIb.

It is interesting to note that the azide symmetric vibration, found at about 2155 to 2165 cm.$^{-1}$, in both the phosphonic mono- and diazides of this study was observed to be little effected by environmental changes. This is also the same frequency that was previously observed for the diarylphosphinic azides.[2] A slight shift to about 2140 cm.$^{-1}$, however, was noted for the azidophosphoranes (IIIa and b) and, as described above, was accompanied by a marked decrease in chemical reactivity of the azide function in these compounds.

Experimental Section

The infrared spectra were determined on a Perkin-Elmer Model 21 spectrophotometer. Molecular weights were determined using the Neumayer thermistor method.[5] Boiling and melting points are not corrected. Volumes of nitrogen are always corrected unless otherwise noted. All azide reactions were carried out under an inert atmosphere and in anhydrous solvents. *CAUTION!* Certain of these azides are shock and heat sensitive and should be handled with extreme care.

Preparation of Azides. Phenylphosphonic Diazide (IIa).—From a batch of phenylphosphonic diazide prepared by stirring overnight 14.5 g. (0.0743 mole) of phenylphosphonic dichloride with 9.7 g. (0.149 mole) of sodium azide in 85.1 g. of dry pyridine, a 10.4-g. aliquot of the solution was removed. Assuming complete conversion to the phosphonic diazide, this sample should yield about 1.6 g. of product after removal of the solvent. The weight of yellow diazide was about 1.6 g. The crude azide was distilled in a bulb-to-bulb apparatus to give a colorless, mobile liquid, b.p. 72–74° (0.1 mm.), $n^{20}\text{D}$ 1.5690. The infrared spectrum of this material had the following principal absorptions: 2164 (vs), 1600 (w), 1443 (m), 1290–1234 (vs), and 1124 (s) cm.$^{-1}$.

Anal. Calcd. for $C_6H_5N_6OP$: N, 40.38; P, 14.88. Found (crude): N, 37.7; P, 15.0. Found (distilled): N, 40.0; P, 14.9.

A drop of distilled material when placed in a bunsen flame "verpufft" while several drops on an anvil exploded with a sharp report when hit several times with a hammer. Samples were detonated at 50, 25, and 20 cm. by a 2-kg. weight in the Olin Mathieson drop-test apparatus. Solutions of the phenylphosphonic diazide in pyridine (15.5 g./85.1 g., respectively) were found not to be shock sensitive.

Phenylthiophosphonic Diazide (IIb).—After stirring overnight, a 10-ml. aliquot was removed from a preparation of phenylthiophosphonic diazide prepared from 13.8 g. (0.065 mole) of phenylthiophosphonic dichloride and 8.5 g. (0.13 mole) of sodium azide

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[4] Similar results have been obtained with diphenylsilyl azidochloride and triphenylphosphine will be the subject of an additional paper by R. A. Baldwin and M. T. Cheng.

[5] J. J. Newmayer, *Anal. Chim. Acta*, **20**, 519 (1959).

in 30 ml. of pyridine. Removal of the pyridine at reduced pressure left 3.9 g. of a brown liquid containing solids.

Distillation of the liquid at 0.1 mm. was attempted using a water bath as the heating medium. Although as the temperature of the bath was slowly increased, little liquid distilled, and solids began to form on the walls above the level of the bath. At some point above 80°, the last recorded temperature, the distillation detonated. The small bulb-to-bulb distillation apparatus was completely demolished. No further attempts were made to distil the phenylthiophosphonic diazide. The diazide in pyridine was found not to be detonated by a 2-kg. weight at 50 cm. The diazide was thus prepared in pyridine without incident and used for subsequent reactions. The infrared spectrum of the diazide in pyridine contained a strong azide absorption at 2160 cm.$^{-1}$ and a P═N absorption at 1250–1242 cm.$^{-1}$.

Phenyl-N,N-dimethylaminophosphonic Azide (XIII).—A mixture of 12.2 g. (0.0604 mole) of phenyl-N,N-dimethylaminophosphonic chloride and 4.2 g. (0.065 mole) of sodium azide were allowed to stir overnight in 45 ml. of pyridine. A 10-ml. aliquot was removed and the pyridine was removed at reduced pressure to yield 2.2 g. of crude amino azide. Distillation at 10^{-3} mm. in a small bulb-to-bulb distillation apparatus gave a colorless distillate boiling at 86–88°, $n^{20}\text{D}$ 1.5473. The distilled amino azide showed no shock sensitivity on the drop-test apparatus.

Anal. Calcd. for $C_8H_{11}N_4OP$: Cl, 0.00; N_3, 19.99; P, 14.74. Found: Cl, 0.47; N_3, 21.1; P, 14.5.

Phenylphosphonic Azidochloride (X).—Following the usual procedure, 9.75 g. (0.05 mole) of phenylphosphonic dichloride and 3.25 g. (0.05 mole) of sodium azide in 30 ml. of pyridine were stirred at ambient temperature for 18 hr. A 10-ml. aliquot was concentrated at reduced pressure to yield 3.0 g. of a cloudy liquid. Distillation at reduced pressure yielded a liquid–solid mixture, b.p. 65–67° at about 0.75 mm., which had $n^{20}\text{D}$ 1.5636. Although the mixture did not "verpufft" when placed in a bunsen flame, it did burn quite vigorously. Furthermore, the sample did not detonate when a 2-kg. weight was dropped from 50 cm. Infrared examination of the solid–liquid mixture showed a strong azide absorption at 2165 cm.$^{-1}$ and a P═N absorption at about 1260 cm.$^{-1}$. Owing to the heterogeneous nature of the distillate, no attempt was made to analyze it. The remaining quantity of the phenylphosphonyl azidochloride was used for subsequent reactions.

N,N′-Phenylphosphonylbis(P,P,P-triphenyliminophosphorane) (IVa).—A mixture of approximately 3 g. (0.0462 mole) of sodium azide and 4.4 g. (0.0226 mole) of freshly distilled phenylphosphonic dichloride [b.p. 135–136° (16 mm.), $n^{20}\text{D}$ 1.5598] in 36 g. of pyridine (dried over calcium hydride) was stirred at ambient temperature for 18 hr. To the resulting pink reaction mixture was slowly added at room temperature 11.9 g. (0.0452 mole) of triphenylphosphine dissolved in 18.3 g. of pyridine. The initial reaction and evolution of nitrogen was rapid; approximately 498 cc. (corrected) of nitrogen (47.6% of theory) was collected in 15 min. At this point, however there was a noticeable decrease in the rate of nitrogen evolution and as a result the mixture was brought to reflux to continue a slow evolution of nitrogen. At this point the reaction mixture still contained a strong azide absorption at 2138 cm.$^{-1}$. After 10 hr. at the reflux temperature, this azide absorption was extremely weak.

The pyridine was decanted from the solids and concentrated at reduced pressure to yield, after digestion with isopropyl alcohol, 12.5 g. (0.085 mole, 81.9% yield) of the product bisphosphorane IVa, m.p. 185–190°. An analytical sample was recrystallized from ethylene glycol dimethyl ether to give a white crystalline material, m.p. 192–193°.

Anal. Calcd. for $C_{42}H_{35}N_2OP_3$ (676.6): C, 74.55; H, 5.21; N, 4.14; P, 13.73. Found: C, 73.82; H, 5.21; N, 3.93; P, 13.6.

A 0.7288-g. (0.00107-mole) quantity of the crude bisphosphorane was stirred with aqueous sodium hydroxide for 24 hr. The solids were filtered, washed with water, and vacuum dried to give 0.7119 g. (about 97.7% recovery) of bisphosphorane melting at 188–192°.

N-(P′-Azidophenylphosphonyl)-P,P,P-triphenyliminophosphorane (IIIa). A. From Phenylphosphonic Diazide.—As described in the previous experiment, 4.7 g. (0.0179 mole) of triphenylphosphine (recrystallized from isopropyl alcohol) dissolved in 7.3 g. of dry pyridine was added to the phenylphosphonic diazide prepared from 3.5 g. (0.0179 mole) of phenylphosphonic dichloride and 2.5 g. (0.0385 mole) of sodium azide in 30.8 g. of pyridine. The reaction was exothermic and 412 cc. (corrected) of nitrogen, representing 51.35% of the total nitrogen or 102.7% of the nitrogen expected by reaction of only one of the azide groups, was collected in 10 min. Again, a sample withdrawn at this point for infrared examination showed an intense azide absorption at 2138 cm.$^{-1}$.

A 10.7-g. quantity of the pyridine solution was removed and concentrated at reduced pressure at ambient temperature to give about 2.1 g. of a cream-colored solid. Then to another 9.8-g. quantity of the pyridine solution was added 3 ml. of anhydrous methanol. The solution was warmed briefly on the steam bath and then concentrated at reduced pressure to yield 1.9 g. of an off-white solid, m.p. 110–126°. Examination of both solids by infrared spectroscopy showed each to have a strong azide absorption at 2137 cm.$^{-1}$, P═N at 1333–1242 cm.$^{-1}$, and P–O at 1205–1198 cm.$^{-1}$. The second, methanol-treated sample had only a weak absorption at 1036 cm.$^{-1}$ due to a $P-O-CH_3$ function. A sample of the crude azidophosphorane was recrystallized from isopropyl alcohol to give white crystals, m.p. 143–145°.

Anal. Calcd. for $C_{24}H_{20}N_4OP_2$: C, 65.16; H, 4.56; P, 14.00; mol. wt., 442. Found: C, 65.43; H, 4.55; P, 14.1; mol. wt., 438.

To the remaining salt and pyridine solution was added 5 ml. of water in an effort to hydrolyze the azidophosphorane to the corresponding phosphonic acid phosphorane VIb. The mixture became cloudy and after 30 min. an additional 10 ml. of water was added, causing a white solid to precipitate. After stirring another hour, the mixture was filtered to yield, after vacuum drying, 2.3 g. of a white powder, m.p. 148–150°. The infrared spectrum of this material was identical with that of the previously obtained azide phosphorane, having a strong azide absorption at 2138 cm.$^{-1}$.

An additional quantity of the azidophosphorane, about 2.1 g. (~0.005 mole), was stirred overnight with aqueous sodium hydroxide. Since the sample had not dissolved in this time, it was heated on a steam bath for 8 hr. without solution taking place. The sample was filtered, washed with water, and vacuum dried to yield 2.1 g. (~100% recovery) of azidophosphorane melting at 140–145°. The slightly low and wide melting point indicated some impurity although the infrared spectrum was unchanged.

B. From N-(P′-Chlorophenylphosphonyl)-P,P,P-triphenyliminophosphorane (XI).—A 5.2-g. (0.02-mole) quantity of triphenylphosphine in 13 ml. of pyridine was added to a pyridine (20 ml.) solution of 3.9 g. (0.02 mole) of phenylphosphonic dichloride and 1.3 g. (0.02 mole) of sodium azide which had been stirred at room temperature for 18 hr. The exothermic reaction yielded 444 cc. (corrected, calcd. 448 cc.) of nitrogen. At this point, the reaction mixture contained only a weak azide absorption at 2137 cm.$^{-1}$ in the infrared.

After the addition of a second 1.3-g. (0.02-mole) quantity of sodium azide, the mixture was sampled periodically for infrared examination which showed the conversion to be complete in approximately 6.5 hr. After the final sampling, the pyridine reaction mixture was poured into 350 ml. of water with stirring. The resulting white precipitate of the azidophosphorane IIIa was filtered and vacuum dried to give 8.6 g. (0.0194 mole, 97.7% yield) having a melting point of 142–145°.

Attempted Thermolysis of IIIa.—A 1.3740-g. (0.00310-mole) sample of the azide phosphorane was slowly warmed from 90 to 200° over 2.25 hr. in a system designed for collection of any offgases. Although the sample appeared to lose 0.0104 g. in weight there was no evolution of nitrogen and infrared examination showed little change in the spectrum. The azide absorption at 2138 cm.$^{-1}$ was still present while a new absorption at about 940–913 cm.$^{-1}$ was developing. After further heating at 200 to 245° for 5 hr., the brown glass no longer contained the azide absorption.

Anal. Calcd. for $C_{24}H_{20}N_2OP_2$: N, 6.76; P, 14.95; mol. wt., 414.4. Found: N, 4.36; P, 15.2; mol. wt., 979.

N-(P′-Hydroxyphenylphosphonyl)-P,P,P-triphenyliminophosphorane (VIb). A. From IIIa.—A slurry of 1.7 g. (0.00384 mole) of the azidophosphorane IIIa in a water–ethanol mixture (12:15 ml.) containing 0.2 g. (0.005 mole) of sodium hydroxide was stirred overnight before it was refluxed for 2 hr. During the reflux period all the solids dissolved. After cooling and filtration of the precipitate, 0.5 g. (0.00113 mole) of the starting azidophosphorane IIIa, m.p. 145–146°, was recovered.

Acidification of the filtrate with concentrated hydrochloric acid followed by dilution with 50 ml. of water gave 0.6 g. (0.00143 mole) of a white solid which softened at 188° and melted at 196–199°. Examination of the infrared spectrum of this material showed the absence of any azide absorption at 2138 cm.$^{-1}$ and the presence of the broad absorptions due to phosphonic acids in the region 2500–1600 and at 940 cm.$^{-1}$. In addition, this material also had a slightly changed phosphorane absorption at about 1250 cm.$^{-1}$ as well as P–C and P-phenyl at 1440 and 1115 cm.$^{-1}$, respectively.

The acid was dissolved a second time in alcoholic sodium hydroxide and acidified to give 0.5 g. of white solid, m.p. 197–199°. A neutralization equivalent of 431 (calcd. 417) was obtained.

B. From XI.—To the pyridine solution of phenylphosphonic azidochloride formed by the *in situ* reaction of 9.75 g. (0.05 mole) of phenylphosphonic dichloride and 3.25 g. (0.05 mole) of sodium azide in 50 ml. of pyridine was slowly added 13.1 g. (0.05 mole) of triphenylphosphine dissolved in 25 ml. of pyridine. The exothermic reaction was cooled by means of an ice–water bath during the addition of the tertiary phosphine (30 min.) and then refluxed for 1 hr. to complete the reaction. The nitrogen evolved was 1117 cc. (calcd. 1120 cc.). The infrared spectrum of the pyridine reaction solution showed the loss of the azide absorption at 2174 cm.$^{-1}$ which had been present in the pyridine solution of the phosphonic azidochloride.

When a portion of the reaction mixture was poured into water, first an oil and then a solid was formed. Recrystallization from methanol and water gave a white crystalline precipitate, m.p. 205–206°. The yield of crude acid was 17.7 g. (0.0424 mole, 84.8%).

Anal. Calcd. for $C_{24}H_{21}NO_2P_2$: C, 69.06; H, 5.07; P, 14.84; neut. equiv., 417. Found: C, 68.91; H, 5.51; P, 14.6; neut. equiv., 413.

N-(P′-Methoxyphenylphosphonyl)-P,P,P-triphenyliminophosphorane (VIa).—Since the previous attempted methanolysis of the azidophosphorane was not successful, another 10.2 g. of the reaction solution and 3 ml. of anhydrous methanol was heated at reflux for 1.5 hr. Concentration at reduced pressure gave an oil which slowly solidified to 3.1 g. of off-white methyl ester VIa. This material contained only a slight azide absorption at 2138 cm.$^{-1}$ while the absorption at 1036 cm.$^{-1}$ due to P–O–CH_3 was now strong. A sample recrystallized from ethylene glycol dimethyl ether and pentane first oiled and then solidified to a white powder, m.p. 133–135°.

Anal. Calcd. for $C_{25}H_{23}NO_2P_2$: N, 3.25; P, 14.36; mol. wt., 431.4. Found: C, 3.45; P, 14.2; mol. wt., 413.

N-(P′-Diethylaminophenylphosphonyl)-P,P,P-triphenyliminophosphorane (VId).—A slurry of 1.6 g. (0.0036 mole) of the azidophosphorane IIIa and 10 ml. of diethylamine (dried over calcium hydride) was allowed to stir for 1.75 hr. at room temperature. After an additional 3.5 hr. at reflux, the reaction mixture was cooled and filtered, and the solids were well washed with water. After vacuum drying overnight, the white solids, 1.5 g., melted at 146–148°. The melting point for the starting azidophosphorane is 144–146°. The infrared spectrum also was identical with that of the azidophosphorane IIIa.

In a second experiment, 1.5 g. (0.0034 mole) of the azidophosphorane IIIa and 5 ml. of diethylamine in 10 ml. of pyridine were refluxed for 6.5 hr. and then stirred for an additional 24 hr. The solvent was removed at reduced pressure to yield a viscous brown oil which solidified on standing for 6 days. The solid was extracted with hot water to give 1.4 g. of a light tan solid, m.p. 108–113°. Recrystallization from hexane and Norit A provided only 0.4 g. (0.00084 mole, 25% yield) of an analytical sample, m.p. 119–120.5°.

Anal. Calcd. for $C_{28}H_3N_2O_2P_2$: C, 71.17; H, 6.40 Found: C, 71.07; H, 6.58.

N-(P′-Anilinophenylphosphonyl)-P,P,P-triphenyliminophosphorane (VIc). A. From IIIa.—A solution of 1.2 g. (0.00271 mole) of azidophosphorane IIIa and 0.4 g. (0.0043 mole) of aniline in 10 ml. of pyridine was stirred at room temperature for 2.5 days. At the end of this period, the azide absorption at 2138 cm.$^{-1}$ was still strong. After refluxing for 24 hr. and adding 0.8 g. more of aniline, the mixture still contained an azide absorption.

The addition of 20 ml. of water caused an oil to separate. The water, pyridine, and excess aniline were then removed at reduced pressure to give a tacky, brown residue. After digestion with acetonitrile and then recrystallization from acetonitrile, 0.2 g. of white, crystalline product, m.p. 208–210°, was obtained.

Anal. Calcd. for $C_{30}H_{26}N_2OP_2$: C, 73.16; H, 5.32. Found: C, 73.25; H, 5.11.

B. From XI.—To a pyridine solution thought to contain 0.0184 mole of the chlorophosphorane XI was added 2 ml. of aniline. The mixture was then refluxed 6 hr. and left to stir overnight. Removal of the pyridine and excess aniline at reduced pressure gave a tacky, brown residue. Digestion with and a recrystallization from acetonitrile yielded 3.3 g. (0.0067 mole, 36.4% yield) of the anilinophosphorane VIc, m.p. 205–210°C.

N,N′-Phenylthiophosphonylbis(P,P,P-triphenyliminophosphorane (IVb).—A 20-ml. quantity of pyridine containing about 7.35 g. (0.0327 mole) of phenylthiophosphonic diazide was added to 17.1 g. (0.0654 mole) of triphenylphosphine dissolved in 25 ml. of pyridine. The initially rapid and exothermic nitrogen evolution had almost stopped after 30 min. with about 720 cc. of nitrogen collected (calcd. 1465 cc.). The reaction was then refluxed overnight to complete the evolution of nitrogen. Removal of the solvent at reduced pressure yielded a tacky, brown residue, which on digestion with isopropyl alcohol became granular. During the digestion, the mixture was spilled which resulted in the recovery of only 9.5 g. (0.0137 mole, 42% yield) of bisphosphorane IVb, m.p. 180–190°.

An analytical sample was recrystallized first from ethylene glycol dimethyl ether and then from acetonitrile to give white crystalline bisphosphorane IVb, m.p. 195–197°.

Anal. Calcd. for $C_{42}H_{35}N_2P_3S$: C, 72.82; H, 5.09; P, 13.41; S, 4.63; mol. wt., 692.7. Found: C, 72.94; H, 5.18; P, 13.3; S, 4.57; mol. wt., 704.

Hydrolysis studies for 24 hr. in aqueous sodium hydroxide and in aqueous sulfuric acid showed this material to be recovered in 96.6 and 94.4% yield, respectively, with only a slight depression in the melting point.

N-(P′-Azidophenylthiophosphonyl)-P,P,P-triphenyliminophosphorane (IIIb).—A 16-ml. quantity of pyridine containing about 6.3 g. (0.028 mole) of phenylthiophosphonic diazide was added to 7.3 g. (0.028 mole) of triphenylphosphine dissolved in 12 ml. of pyridine. The exothermic reaction yielded 600 cc. (calcd. 629 cc.) of nitrogen after 1 hr. at reflux. The infrared spectrum of the pyridine solution contained a strong azide absorption at 2141 cm.$^{-1}$ as well as a broad, strong P=N absorption at 1242–1220 cm.$^{-1}$. Dilution of a 10-ml. aliquot of the reaction mixture with 30 ml. of water gave an oil. The pyridine and water were decanted and the oil was dried at reduced pressure to give a tacky, clear residue which could not be induced to crystallize. Infrared examination of the residue in benzene showed a strong azide absorption at 2141 cm.$^{-1}$ and no evidence of hydrolysis. The remaining solution of the azidophosphorane IIIb was used for subsequent reactions.

N-(P′-Methoxyphenylthiophosphonyl)-P,P,P-triphenyliminophosphorane (V).—Methanol, 5 ml., was added to the solution remaining from the preparation of azidophosphorane IIIb which contained approximately 0.02 mole of the starting material. It was necessary to reflux the reaction mixture for about 36 hr. in order to complete the reaction (as followed by infrared spectroscopy). After removal of the solvent at reduced pressure and digestion with methanol, 4.5 g. (0.01 mole, 50% yield) of the desired methoxythiophosphorane V was recovered. Recrystallization from methanol and Norit A gave an analytical sample melting at 121–123°.

Anal. Calcd. for $C_{25}H_{23}NOP_2S$: N, 3.13; P, 13.84; S, 7.16. Found: N, 3.17; P, 14.1; S, 7.02.

N-(P′-Dimethylaminophenylphosphonyl)-P,P,P-triphenyliminophosphorane (XIV).—A 6.1-g. (0.03-mole) quantity of phenyl-N,N-dimethylaminophosphonic chloride [b.p. 92° (0.2 mm.), n^{20}D 1.5477] and 1.95 g. (0.03 mole) of sodium azide was allowed to stir overnight at ambient temperature. The addition of 7.9 g. (0.03 mole) of triphenylphosphine dissolved in 25 ml. of pyridine at ambient temperature resulted in the slow evolution of nitrogen which was incomplete after stirring for 23 hr. After 1.5 hr. at reflux, the collected nitrogen was 672 cc. (corrected, 100% of theory). The pink pyridine reaction mixture was poured into 500 ml. of water which caused a white precipitate to form. The solids were filtered, vacuum dried overnight, and then washed with ether to give 12.4 g. (0.0279 mole, 93% yield) of a white powder, m.p. 126.5–129°.

Anal. Calcd. for $C_{26}H_{26}N_2OP_2$: C, 70.26; H, 5.90; N, 6.30; P, 13.94; mol. wt., 444.4. Found: C, 69.72; H, 6.01; N, 5.94; P, 14.0; mol. wt., 436.

A 2.1479-g. (0.00483-mole) quantity of the aminophosphorane XIV was dissolved in 10 ml. of ethanol and 2 ml. of water containing 3 ml. of concentrated hydrochloric acid. The solution was then stirred for 1 hr., refluxed for 1 hr., and then left to stir at ambient temperature for 14 hr. Removal of the solvents on a Rinco evaporator using an aspirator gave a gummy, white residue. Digestion with methanol resulted in the crystallization of the residue to yield 1.0566 g. (0.0253 mole, 52.4% yield) of the acid Vb, m.p. 205–208°, m.m.p. 206–208° with authentic acid. The remaining methanol-soluble portion was further refluxed with hydrochloric acid for 5 hr. to yield a yellow oil which did not crystallize.

The attempted acid cleavage of the aminophosphorane XIV was carried out by passing dry hydrogen chloride into a slurry of 2.2 g. (0.005 mole) of the compound in 20 ml. of benzene until no further absorption was observed. The solids became tacky as the addition continued. Excess hydrogen chloride was removed by adding pyridine which caused the precipitation of pyridine hydrochloride. The solids were removed by filtration under dry nitrogen and the benzene–pyridine solution was concentrated to yield a white, tacky residue. That this residue was not the chlorophosphorane was shown by the fact that when it was dissolved in pyridine and then poured into water, the crystalline acidic phosphorane VIb expected from the hydrolysis of the chlorophosphorane XI was not isolated. Only a tacky residue which could not be crystallized was obtained.

Reaction of Phenylphosphonic Diazide (IIa) and 1,4-Bis(diphenylphosphino)benzene (VII).—A 12.9-g. (0.0288-mole) quantity of 1,4-bis(diphenylphosphino)benzene was slurried with 35 ml. of pyridine, and the addition of 40 ml. of the previously prepared pyridine solution of phenylphosphonic diazide was begun at room temperature. The reaction was exothermic and after 30 min. the reaction mixture began to clear up, the solution being complete in 1 hr. At this point the reaction had slowed noticeably, with 625 cc. (corrected) of nitrogen representing 48.35% of the total nitrogen being collected. An infrared examination of the pyridine solution removed at this time showed a strong azide absorption at 2138 cm.$^{-1}$ and a general similarity to the previously isolated azide phosphorane. A 10-ml. (~10.5-g.) aliquot of the reaction solution was removed and 40 ml. of water was added. The resulting pale yellow solid weighed approximately 1.5 g. After drying and standing for several days, the sample was examined by infrared spectroscopy. The expected strong azide absorption at 2138 cm.$^{-1}$ was found to be weak, instead, while the remaining absorptions characteristic of the phosphorane portion of the spectra were present, *i.e.*, absorptions at 1439 (m), 1205 (sb), and 1117 (s) cm.$^{-1}$.

The remaining reaction solution was then brought to reflux to force the formation of polymeric phosphorane. After 4 hr., an additional 630 cc. of nitrogen was collected. The total nitrogen collected was 1255 cc. (calcd. 1292 cc.). A sample of the clear, yellow-brown solution was removed for infrared examination. A weak azide absorption at 2138 cm.$^{-1}$ was observed. Removal of the pyridine at reduced pressure gave approximately 16.0 g. of a tan powder which softened at 94°, foamed from 105 to 130°, and appeared to be completely liquid at 165°. A small sample placed on the high vacuum line and heated to 140° in 1 hr. appeared to soften and melt at 160–170°. Differential thermal analysis showed only a broad indistinct melting range at 136 ± 20° and the first transition or decomposition point at about 477°.

Anal. Calcd. for VIII: N, 4.68; P, 15.50. Found: N, 3.58–4.25; P, 14.2–15.2; mol. wt., 2300.

Attempted Isolation of IXa.—A 20-ml. quantity of a pyridine solution containing about 4.8 g. (0.023 mole) of phenylphosphonic diazide was added to 10.2 g. (0.023 mole) of 1,4-bis(diphenylphosphino)benzene in 20 ml. of pyridine. The exothermic reaction evolved 544 cc. (corrected, 106%) of nitrogen in 45 min. When the reaction mixture was poured into 175 ml. of water, an oil separated. After stirring for 2 hr. and cooling in an ice bath, the oil did not solidify.

The major portion of the oil was skimmed off the water and dried at reduced pressure overnight. The resulting yellow-brown foam weighed 11.7 g. Infrared examination of the foam showed a very weak azide absorption at 2137 cm.$^{-1}$ in addition to typical phosphorane absorptions and perhaps P–O–P absorption at 930 cm.$^{-1}$. In spite of the seemingly weak azide absorption in the infrared, the phosphorus value was in good agreement for IXa. (*Anal.* Calcd. for $C_{36}H_{29}N_4OP_3$: P, 14.83. Found: P, 14.8.) However, when a sample of this material was heated at reflux in pyridine, no further nitrogen was evolved. This implied that the phosphorus value was in error and that polymerization had occurred during the work-up.

The solvent was again removed at reduced pressure to yield an almost white foam which was dried at 0.3 mm. and 100° for 6 hr. (*Anal.* Found: N, 3.58; P, 15.0.) A 3.9-g. quantity of this dried material was extracted for 4 hr. at ambient temperature with 30 ml. of benzene and then on the steam bath for 10 min. After cooling, the clear benzene layer was decanted from the brown insoluble material and the benzene was carefully removed at reduced pressure to give (after drying at 100° and 0.3 mm. for 2 hr.) 1.9 g. of white powder.

Anal. Calcd. for VIII $C_{36}H_{29}N_2OP_3$: C, 72.24; H, 4.88; N, 4.68; P, 15.52. Found: C, 70.71; H, 4.94; N, 3.37; P, 15.0; mol. wt., 1855.

The brown, insoluble fraction (1.4 g.) was similarly dried and analyzed. (*Anal.* Found: C, 71.23; H, 5.08; N, 3.78; P, 15.3.) Differential thermal analysis curves for both of these fractions appeared to indicate a beginning of decomposition at about 455°. Broad endotherms were observed at about 550°.

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Ring-Size Effects in the Pinacol Rearrangement

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One general ring-size effect was observed in the rearrangement of (1-hydroxycyclohexyl)phenylcarbinol (**1**), (1-hydroxycyclopentyl)phenylcarbinol (**2**), (1-hydroxycyclohexyl)methylphenylcarbinol (**3**), and (1-hydroxycyclopentyl)methylphenylcarbinol (**4**) in concentrated sulfuric acid. The five-membered ring compounds gave more ring expansion than the six-membered analogs. An interpretation of this result is offered and its bearing on the mechanism of the rearrangement is discussed.

In a recent paper[2] from this laboratory it was shown that the product distribution from the pinacol rearrangement of cyclopentylcyclohexane-1,1′-diol (**5**) could not be rationalized by the simple application of the I-strain theory.[3] That is the formation of a carbonium ion (or S$_N$2 intermediate) on the five-membered ring should be favored over the same reaction on the six-membered ring by changes in the strain owing to

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[2] R. D. Sands and D. G. Botteron, *J. Org. Chem.*, **28**, 2690 (1963).

[3] H. C. Brown, J. H. Brewster, and H. Schechter, *J. Am. Chem. Soc.*, **76**, 467 (1954).