Table IV. Activation Parameters at 25°

	ΔH^*, kcal/mole	ΔS^*, eu	S^* (complex),[19] eu	Ref
$NpO_2^+ + Cr^{2+} + H^+ = (H \cdot NpO_2 \cdot Cr^{4+})^*$	1.85	−38	−66	This work
$NpO_2^+ + Fe^{2+} + H^+ = (H \cdot NpO_2 \cdot Fe^{4+})^*$	8.6	−38	−69	20
$VO_2^+ + Fe^{2+} + H^+ = (H \cdot VO_2 \cdot Fe^{4+})^*$	1.52	−37	−70	19
$NpO_2^+ + Np^{3+} + H^+ = (H \cdot NpO_2 \cdot Np^{5+})^*$	5.9	−31	−72	16

inner-sphere structure has direct experimental evidence only in the case of the first entry. All of these reactions listed are characterized by low heats of activation, but this is especially true in the V(V)–Fe(II) and Np(V)–Cr(II) reactions. The ΔS^* values for the first three reactions are in remarkable agreement, and the surprising correlation between the charge of the activated complex and the associated S^* value as noted by Newton and Rabideau[24] for actinide elements is followed by the Np(V)–Cr(II) reaction. The Np(V)–Np(III) system has a S^* value expected for +4 charged activated complexes rather than those with +5 charge. The results presented in this paper suggest that some of this discrepancy may be due to the contribution by a path independent of (H^+), at least at ($HClO_4$) ≤ 0.2 *M*.

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[24] T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).

Phosphiran[1a]

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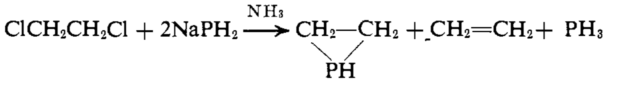
Abstract: The novel heterocycle phosphiran (phosphacyclopropane) has been prepared by two routes. It has been characterized by mass, infrared, and nuclear magnetic resonance spectra. Phosphiran is thermally unstable and decomposes to a viscous, involatile liquid.

The preparation of phosphiran (phosphacyclopropane, **1**) has been briefly described,[2] but no details of its characterization or of its spectral properties have yet appeared. The present paper describes in detail both the original preparation of the heterocycle[2] and a novel preparative method and describes its characterization and some of its properties.

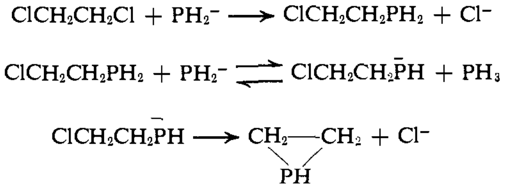
During the course of some further work on phosphorus–boron polymer chemistry,[3] an attempt was made to prepare 1,2-diphosphinoethane by reaction between 1,2-dichloroethane and phosphinide ion in anhydrous ammonia. The reaction did not follow the nucleophilic substitution pathway usually observed with simple alkyl halides, but yielded phosphiran, phosphine, and ethylene.



$$ClCH_2CH_2Cl + 2NaPH_2 \xrightarrow{NH_3} \underset{\text{PH}}{CH_2{-}CH_2} + CH_2{=}CH_2 + PH_3$$

1

A tentative mechanism for this ring-closure reaction is



$$ClCH_2CH_2Cl + PH_2^- \longrightarrow ClCH_2CH_2PH_2 + Cl^-$$

$$ClCH_2CH_2PH_2 + PH_2^- \rightleftharpoons ClCH_2CH_2\bar{P}H + PH_3$$

$$ClCH_2CH_2\bar{P}H \longrightarrow \underset{\text{PH}}{CH_2{-}CH_2} + Cl^-$$

The reaction is efficient and has yielded up to 74% of phosphiran based on starting 1,2-dichloroethane. Unusual reactions between phosphinide ions and vicinal dihaloalkanes have been reported by other workers[4] although the phosphorus-containing products which were obtained were quite different from those reported here

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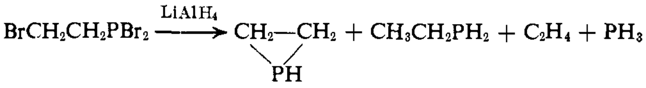
[2] R. I. Wagner, U. S. Patent 3,086,056 (1963).

[3] A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953).

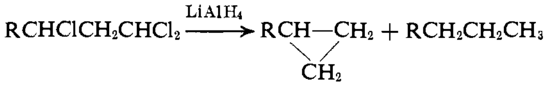
[4] K. Issleib and K. Stanktke, *Ber.*, **96**, 279 (1963).

A second route to phosphiran is the lithium aluminum hydride reduction of 2-bromoethylphosphonous dibromide.[5] This reaction proceeds smoothly in diethylene glycol diethyl ether to give a mixture of phosphiran, ethylphosphine, ethylene, and phosphine. Phosphiran can conveniently be separated from ethylphosphine by gas–liquid chromatography. This reduction is formally analogous to the reduction of 1,1,3-trichloroalkanes with lithium aluminum hydride, which yields a mixture of alkylcyclopropane and alkane.[6]



$$BrCH_2CH_2PBr_2 \xrightarrow{LiAlH_4} \underset{PH}{CH_2{-}CH_2} + CH_3CH_2PH_2 + C_2H_4 + PH_3$$

Cf.



$$RCHClCH_2CHCl_2 \xrightarrow{LiAlH_4} \underset{CH_2}{RCH{-}CH_2} + RCH_2CH_2CH_3$$

The vapor density molecular weight of phosphiran is 60, and this is confirmed by its mass spectral molecular weight (see Table I). The boiling point of phosphiran is 36.5°, somewhat higher than that of ethylphosphine (25°). This is parallel to the behavior of thiiran, bp 55°, and ethanethiol, bp 37°. The Trouton constant for phosphiran is 22.3 cal/deg mole, indicating that it is not a strongly associated liquid.

Table I. Mass Spectrum of Phosphiran[a]

m/e	Relative abundance	Probable ion
60	100.0	$C_2H_5P^+$
58	62.2	$C_2H_3P^+$
57	55.8	$C_2H_2P^+$
56	17.0	C_2HP^+
45	29.8	CH_2P^+
44	10.2	CHP^+
34	13.2	PH_3^+
29	13.0	$C_2H_5^+$
28	20.0	$C_2H_4^+$
27	30.5	$C_2H_3^+$
26	11.0	$C_2H_2^+$

[a] Determined on a Hitachi Perkin-Elmer RMU-6D mass spectrometer at 80 ev. All peaks of intensities greater than 10% of the parent peak at m/e 60 are given.

The mass spectrum of phosphiran is given in Table I. There have been few mass spectral studies of organophosphorus compounds, but the mass spectra of some simple alkylphosphines have been described.[7] Many of the features of the mass spectrum of phosphiran are analogous to those reported for alkylphosphines. For example, the ions PH_3^+, CHP^+, and CH_2P^+ are observed in the mass spectra of trimethylphosphine and ethylphosphine.

The infrared spectrum of phosphiran vapor shows absorption at 3088 and 3010 cm^{-1}, attributable to a C–H stretching frequency in a small strained ring, and near those observed in cyclopropane, oxiran, thiiran, and aziridine.[8] The P–H stretching band at 2287 cm^{-1} is strong and has the same symmetrical shape as has been noted for other secondary phosphines. The intense P–H deformation band appeared at 1004 cm^{-1} with rotational p and r maxima separated by 25 cm^{-1}. There is also a series of bands around 1000 cm^{-1} which may be assigned to ring vibrations. The absence of a pattern of bands at about 1595, 1392, and 1262 cm^{-1}, characteristic of P-vinyl compounds,[9] further favors the phosphiran formulation rather than the isomeric vinylphosphine.

The nuclear magnetic resonance (nmr) spectra of phosphiran are remarkable. The ^{31}P nmr spectrum consists of a doublet, centered at +341 ppm from external 85% H_3PO_4, with J_{P-H} = 155 cps. Each component of this doublet is further split in a complex manner by interaction with protons attached to carbon.[10] The phosphorus chemical shift is the highest reported for a phosphine and is apparently exceeded among phosphorus compounds only by the molecule P_4 (δ 488 ppm in CS_2),[11] another molecule containing strained, three-membered, rings. The phosphorus–hydrogen coupling constant is unusually small for a phosphine and falls between those reported for phosphinide ion, PH_2^-, where J_{P-H} = 138 cps,[12] and phosphine itself, PH_3, where J_{P-H} = 182 cps.[11] The ^1H nmr spectrum shows a complex multiplet at 0.47–1.50 ppm downfield from $(CH_3)_4Si$, of total relative intensity 9, and an approximate quintet upfield from $(CH_3)_4Si$, of relative intensity 1. The downfield multiplet is assignable to the protons attached to carbon, plus half of the signal due to the proton attached to phosphorus, while the upfield multiplet is assignable to the other component of the signal due to the proton attached to phosphorus. By using the J_{P-H} derived from the ^{31}P nmr spectrum, the center of the ^1H nmr doublet due to the proton attached to phosphorus is estimated to be at 0.47 ppm upfield from $(CH_3)_4Si$. The complexity of the C–H region in the ^1H nmr spectrum suggests that the spectrum is of the AA′BB′MX type, and that the hydrogen on phosphorus is neither exchanging nor inverting rapidly on the nmr time scale. Presumably the bonding situation in phosphiran is responsible for the unusual nmr parameters.

Phosphiran is thermally unstable in the liquid phase and decomposes completely within 24 hr at 25° to give ethylphosphine (15%), ethylene (6%), plus a viscous nonvolatile liquid. Phosphiran is also rapidly decomposed below room temperature by hydrogen chloride. In this case the products include ethylene (90%), phosphine (20%), a little ethylphosphine (5%), and an involatile yellow solid which, by the stoichiometry of the reaction, is mainly a polymeric phosphorus hydride.

Phosphiran is not rapidly decomposed by methanol at room temperature, and a study of the ^1H nmr spectrum of the solution indicates that the hydrogen on phosphorus is not undergoing rapid exchange with solvent hydrogen atoms. This is in contrast to the behavior of methylphosphine, which does undergo a rapid exchange reaction in methanol solution at room tem-

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(5) B. Fontal and H. Goldwhite, *Chem. Commun.*, 111 (1965).

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(9) H. D. Kaesz and F. G. A. Stone, *Spectrochim. Acta*, 360 (1959).

(10) A full analysis of the nmr spectra is in progress.

(11) E. Fluck, "Die Kernmagnetische Resonanz und ihre Anwendung in der Anorganischen Chemie," Springer-Verlag, Berlin, 1963, pp 256–274.

(12) E. A. V. Ebsworth and G. M. Sheldrick, 8th Congress on Molecular Spectroscopy, Copenhagen, Aug 1965.

perature.[13] This may indicate that phosphiran is a weaker base than methylphosphine and that it is not capable of accepting a proton from the weak acid methanol. It has been previously observed that aziridine is an unusually weak base[14] (pK_a = 8.04) compared with acyclic analogs (*cf.* $(CH_3)_2NH$, pK_a = 10.77) and this may also hold for the analogous phosphorus bases.

In some preliminary attempts to prepare P-substituted phosphirans, the reaction between 1,2-dichloroethane and sodium methylphosphinide has been examined. In addition to methylphosphine and ethylene, a mixture of products containing phosphorus has been obtained. Infrared spectroscopy indicates the presence of methylvinylphosphine and ethylmethylphosphine together with another component which may be the desired P-methylphosphiran. Further study of this reaction and of the chemistry of phosphiran is in progress.

Experimental Section

Volatile materials were handled in a conventional vacuum line. They were separated by fractional condensation or by gas-liquid chromatography. The gas chromatograph was modified so that reactive volatile samples could be introduced onto the column in a current of helium, and so that eluted fractions could be collected in traps cooled in liquid N_2 and transferred to the vacuum line. The chromatograph was equipped with a 20 ft × 0.25 in. column of 10% diisodecyl phthalate on acid-washed Chromosorb W, 60-80 mesh.

Infrared spectra were determined on a Beckman IR-12 spectrophotometer; ^{1}H nmr spectra were determined on a Varian A-60 spectrometer, and ^{31}P nmr spectra were determined on a Varian V-4300B spectrometer with probe operating at 24.3 Mc.

Phosphiran from 1,2-Dichloroethane. 1,2-Dichloroethane (13 mmoles) was condensed at $-196°$ into a tube containing an approximately 1.6 *M* solution of sodium phosphinide (26 mmoles) in ammonia. The rapid exothermic reaction was controlled by periodic cooling of the tube in a $-78°$ bath. The volatile products were isolated as quickly as possible by a combination of mechanical separation of the immiscible liquid phases at $-78°$ and fractional condensation. Phosphine (14 mmoles) and ethylene (1.2 mmoles) were thus separated from phosphiran (10 mmoles) which was retained in a $-100°$ trap. Phosphiran has mp -121.4 to $-120.9°$ (Stock plunger method); vapor tension equation $\log P_{mm} = 7.753 - 1509/T$ (from which were calculated bp = 36.5°, ΔH_v = 6.90 kcal/mole, and Trouton constant = 22.3 cal/deg mole); and vapor density molecular weight 60.0 (calcd for C_2H_5P, 60.0).

Reduction of 2-Bromoethylphosphonous Dibromide. Lithium aluminum hydride (10.0 g) was added slowly to diethylene glycol diethyl ether (200 ml) in a 500-ml three-necked flask fitted with a dropping funnel and reflux condenser and containing a Teflon-coated magnetic stirring bar. A solution of 2-bromoethylphosphonous dibromide[5] (25.0 g, 83.0 mmoles) in diethylene glycol diethyl ether (50 ml) was placed in the dropping funnel. The flask was connected to the vacuum system, evacuated, and cooled to -20 to $-10°$. The hydride mixture was stirred vigorously and the 2-bromoethylphosphonous dibromide solution was cautiously added. A vigorous evolution of gas was observed. The volatile materials produced were passed through a trap cooled to $-80°$ and two traps cooled to $-196°$. Hydrogen was continuously removed by pumping to maintain a pressure of less than 1 mm in the reaction flask. When all the 2-bromoethylphosphonous dibromide solution had been added, the reaction mixture was allowed to attain room temperature, and further volatile material was collected over a period of approximately 2 hr.

The material which had collected in the traps at $-196°$ was fractionated in the vacuum system. The fraction condensing at $-196°$ (0.9 mmole) was shown by infrared spectroscopy to contain mostly phosphine together with a small quantity of ethylene. The fraction condensing at $-95°$ (42.0 mmoles) was shown by infrared and nmr spectroscopy to consist mostly of ethylphosphine and phosphiran.

The $-95°$ fraction, in portions of approximately 1 mmole, was passed through the gas chromatograph at 30°. The helium flow rate was 60 cc/min. Two major fractions were obtained. The largest fraction, identified by infrared spectroscopy as ethylphosphine (2.0 g, 32.0 mmoles), had a retention time of 6 min. A smaller fraction, with a retention time of 13 min, was identified as phosphiran (0.24 g, 4.0 mmoles). In addition there was a small fraction with a very short retention time which was shown by infrared spectroscopy to be a mixture of ethylene and phosphine.

Reaction of Phosphiran with Hydrogen Chloride. Phosphiran (0.054 g, 0.90 mmole) and hydrogen chloride (0.033 g, 0.90 mmole) were condensed at $-196°$ from the vacuum system into a 5-ml, heavy-wall glass reaction tube. The tube was sealed and allowed to warm up slowly. A rapid reaction, with the formation of a yellow solid, was observed below room temperature. The volatile products were taken into the vacuum system, and infrared spectroscopy showed that ethylene was the major product. Phosphine and ethylphosphine together with hydrogen chloride were also present. The hydrogen chloride was removed by shaking the mixture with quinoline (0.5 g) in a sealed reaction tube. Further fractionation in the vacuum system gave (i) a mixture containing phosphine (0.2 mmole) and ethylene (0.8 mmole) condensing at $-196°$ (the approximate proportions of the components of the mixture were estimated from the infrared spectrum) and (ii) ethylphosphine (0.05 mmole). The quantity of hydrogen chloride present in the original mixture was estimated by difference as approximately 0.8 mmole.

Reaction between 1,2-Dichloroethane and Sodium Methylphosphinide. This reaction was carried out on the same scale, and in essentially the same way, as that described above for sodium phosphinide. Fractional condensation yielded methylphosphine (28%) and ethylene (11%) and a mixture of products containing phosphorus (passed $-45°$, trapped $-78°$). Vapor density molecular weights of the head and tail fractions of a 4-mmole sample were 73.8 and 75.1 (calcd for C_3H_7P, 74.0). The infrared spectrum showed bands at 3080 (P-methylphosphiran or methylvinylphosphine ?) 1570, 1390, and 1248 (P-vinyl ?), and 2278 cm^{-1} (methylvinylphosphine or ethylmethylphosphine ?).

Acknowledgments. We thank Dr. M. C. Caserio and Dr. S. L. Manatt for assistance in determining the nuclear magnetic resonance spectra.

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(14) S. Searles, M. Tamres, F. Block, and L. A. Quarterman, *J. Am. Chem. Soc.*, **78**, 4917 (1956).