

method of Cava and Bhattacharya,<sup>29</sup> involving diazotization (HCl) of 6-amino-2-methylpyridine, permanganate oxidation to 6-chloropicolinic acid, and esterification. The ester was treated with methylmagnesium bromide to afford **30** in 85% yield: bp 82–84° (2 mm); nmr (CCl<sub>4</sub>)  $\delta$  1.52 (s, 6), 4.07 (s, 1), and 7.40 (m, 3).

*Anal.* Calcd for C<sub>8</sub>H<sub>10</sub>ClNO: C, 56.00; H, 5.87; N, 8.16; Cl, 20.66. Found: C, 55.89; H, 5.87; N, 7.94; Cl, 20.80.

**2-(6-Chloro-2-pyridyl)-2-chloropropane (31).**—Chloride **31** was synthesized by procedure A. The nmr spectrum of the red oil (2.5 g) showed it to be 30% chloride **31** and 70% 2-(6-chloro-2-pyridyl)propene. The nmr spectrum (CCl<sub>4</sub>) showed resonances at  $\delta$  1.91 (s) and 8.31 (m). The same spectrum showed resonances for the olefin at  $\delta$  2.15 (broad s, 3 H), 5.21 (broad s, 1 H), 5.81 (broad s, 1 H), and 8.31 (m).

**Kinetic Procedures.**—Kinetic procedures have been reported previously.<sup>11,30</sup>

**Registry No.**—**1**, 6581-08-4; **2**, 40472-49-9; **3**, 40472-50-2; **4**, 40472-51-3; **5**, 40472-75-1; **6**, 40472-76-2;

(30) D. S. Noyce and R. W. Nichols, *J. Org. Chem.*, **37**, 4306 (1972).

**7**, 40472-77-3; **8**, 40472-78-4; **9**, 40472-79-5; **10**, 40472-80-8; **11**, 40472-81-9; **12**, 40472-82-0; **13**, 40472-83-1; **14**, 40472-84-2; **15**, 20826-02-2; **16**, 40472-86-4; **17**, 40472-87-5; **18**, 40472-88-6; **19**, 40472-89-7; **20**, 40472-90-0; **21**, 40472-91-1; **22**, 40472-92-2; **23**, 40472-93-3; **24**, 40472-94-4; **25**, 40521-10-6; **26**, 40521-11-7; **27**, 40521-12-8; **28**, 40472-95-5; **29**, 40472-96-6; **30**, 40472-97-7; **31**, 40472-98-8; 2-bromo-5-methylpyridine, 3510-66-5; methyl 4-chloropicolinate, 24484-93-3; 2-bromo-5-chloropyridine, 40473-01-6; ethyl 4-chloro-5-methoxypicolinate, 40473-02-7; ethyl 5-methoxypicolinate, 40473-03-8; 5-methylnicotinic acid hydrochloride, 40473-04-9; ethyl 5-bromonicotinate, 20986-40-7; ethyl 6-methylnicotinate, 21684-59-3; 2-bromo-6-methoxypyridine, 40473-07-2; 2-bromo-6-ethoxypyridine, 4645-11-8.

## CNDO-MO Exploration of Concerted and Stepwise Pathways for the Wittig and Peterson Olefination Reactions

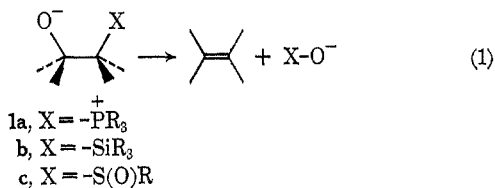
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*Received February 26, 1973*

The decomposition of species of the type XCH<sub>2</sub>CH<sub>2</sub>O<sup>-</sup> to XO<sup>-</sup> and CH<sub>2</sub>=CH<sub>2</sub> was investigated with the aid of CNINDO calculations for the cases where X is H<sub>3</sub>P<sup>+</sup> (Wittig reaction) and H<sub>3</sub>Si<sup>-</sup> (Peterson reaction). Four-center intermediates **2a** (dihydrooxaphosphetane) and **2b** (dihydrooxasiletanide anion) were assumed and energies calculated for these and for the family of structures resulting from cleavage of the C–O and C–X bonds simultaneously (concerted fragmentation) or in separate stages (nonconcerted fragmentation). The calculations indicate that the energy surfaces are sharply skewed with C–X cleavage more advanced than C–O cleavage with the degree of skewing much greater for the Peterson reaction than for the Wittig reaction. The amount of stabilization of **2a** relative to its betaine precursor **1a** is calculated to be greater than that of **2b** relative to its precursor **1b** and it was concluded that dihydrooxaphosphetane **2a** is probably a true intermediate in the Wittig reaction but that dihydrooxasiletanide **2b** may be bypassed in the Peterson process with **1b** going directly to H<sub>3</sub>SiOCH<sub>2</sub>CH<sub>2</sub><sup>-</sup> (**3b**). Examples are given where theory and experiment are in harmony.

Four-center reactions involving intramolecular nucleophilic attack by alkoxide oxygen on a second-row element as a key step are common and provide the basis for a number of mechanistically interesting and synthetically useful olefin syntheses given in general terms by eq 1.



The best known and most widely studied examples of these processes utilize phosphorus as the electrophilic center and include the Wittig reaction and its many modifications.<sup>1</sup> Less well known, but becoming increasingly useful for the synthesis of heteroatom-substituted olefins especially, are the base-catalyzed decomposition reactions of  $\beta$ -hydroxysilanes (the Peterson reaction).<sup>2</sup> In both the silicon and phosphorus cases decomposition of **1** (referred to as the "betaine"

intermediate for **1a**) occurs under extremely mild conditions with the thermodynamic driving force being derived, in large part, from the formation of strong phosphorus–oxygen or silicon–oxygen bonds. The decomposition of  $\beta$ -hydroxy sulfoxides has also been observed<sup>3,4</sup> and a method developed for olefin synthesis employing thermal decomposition of  $\beta$ -hydroxy sulfonamides in benzene or toluene at 80–110°.<sup>5</sup> For each of these fragmentations a syn elimination is conceptually the most attractive and is supported by experiment in those cases which have been studied with respect to stereochemistry.<sup>5,6</sup>

An important question regarding the elimination pathways available to **1a–c** remains unanswered despite the number of studies, both synthetic and mechanistic, of the Wittig and related reactions. That question is concerned with whether thermal uncatalyzed decomposition of **1** is concerted or is rather a multistep process proceeding *via* initial formation of a four-membered ring intermediate. Further, if a four-membered ring species is an intermediate, does it

(1) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Inc., Menlo Park, Calif., 1972, pp 682–709, and references cited therein.

(2) (a) D. J. Peterson, *J. Org. Chem.*, **33**, 780 (1968); (b) T. H. Chan, E. Chang, and E. Vinokur, *Tetrahedron Lett.*, 1137 (1970); (c) F. A. Carey and A. S. Court, *J. Org. Chem.*, **37**, 939, 1926 (1972), and references cited therein.

(3) (a) C. Walling and L. Bollyky, *ibid.*, **28**, 256 (1963); (b) E. J. Corey and M. Chaykovsky, *ibid.*, **28**, 254 (1963).

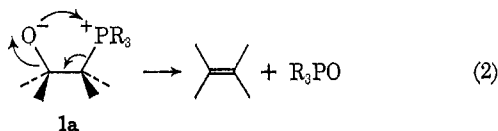
(4) For an analogous process see T. J. Wallace, *ibid.*, **30**, 4016 (1965).

(5) (a) E. J. Corey and T. Durst, *J. Amer. Chem. Soc.*, **90**, 5548, 5553 (1968); (b) T. Durst, *Quart. Rep. Sulfur Chem.*, **3**, 113 (1968).

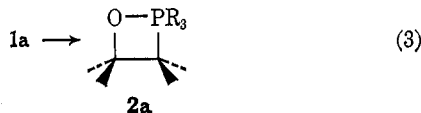
(6) E. Vedejs and P. L. Fuchs, *J. Amer. Chem. Soc.*, **93**, 4070 (1971).

fragment by a concerted or nonconcerted path? These possibilities are represented for the phosphorus case in Chart I. Analogous routes can be considered for the cases which result when X is silicon or sulfur.

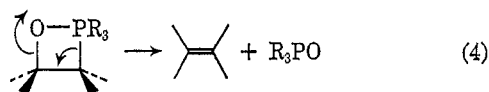
CHART I  
Concerted Decomposition of Betaine



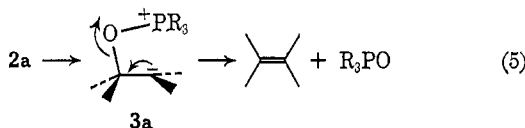
Initial Formation of a Dihydrooxaphosphetane Intermediate



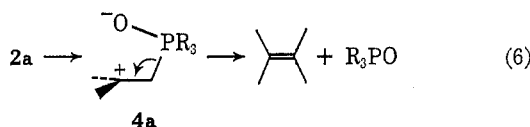
Concerted Decomposition of Dihydrooxaphosphetane



Nonconcerted Decomposition of Dihydrooxaphosphetane (P-C Cleavage)

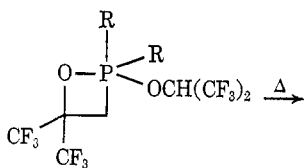


Nonconcerted Decomposition of Dihydrooxaphosphetane (C-O Cleavage)

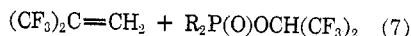


Analogous structures (1b-4b) may be considered for the Peterson process by substituting silicon for phosphorus with appropriate formal charge adjustment.

The experimental evidence available at present does not permit a unique choice to be made among the alternative mechanisms outlined in Chart I. While the observed stereospecific nature of the eliminations<sup>5,6</sup> is readily accommodated by the concerted fragmentation of eq 2 and 4, it would also be possible from a nonconcerted process (eq 5 or 6) if decomposition of the zwitterionic intermediate (3a or 4a) were faster than rotation around the carbon-carbon bond. The intermediacy of the dihydrooxaphosphetane 2a receives support from the recent isolation of such a species and the demonstration of its thermal conversion to olefins and phosphinate esters on heating (eq 7).<sup>7</sup>



5a, R = CH<sub>3</sub>  
b, R = Ph



(7) (a) F. Ramirez, C. P. Smith, and J. F. Pilot, *J. Amer. Chem. Soc.*, **90**, 6726 (1968); (b) M. U. Haque, C. N. Caughlan, F. Ramirez, J. F. Pilot, and C. P. Smith, *ibid.*, **93**, 5229 (1971).

While it could be argued that concerted fragmentation of a dihydrooxaphosphetane to an olefin and a phosphine oxide is similar to the thermally forbidden [ $\sigma_{2s} + \sigma_{2s}$ ]<sup>8</sup> conversion of cyclobutane to two ethylenes, this would not appear to be an apt analogy. Theoretical<sup>9</sup> and experimental<sup>10</sup> results indicate that incorporation of heteroatoms into four-membered rings lowers the activation energy for certain concerted reactions. Further, the expanded coordination and the participation of d orbitals in the bonding scheme renders comparison of dihydrooxaphosphetanes and dihydrooxasiletanide anions with four-membered rings containing only first-row elements suspect. Accordingly, a theoretical study of the various mechanisms was undertaken to determine whether a choice could be made between them.

## Results and Discussion

### General Comments on the Computational Method.—

The symmetry considerations developed by Woodward and Hoffmann are not directly applicable to the systems of this work since these systems lack suitable symmetry elements. The principle of phase continuity (which is an extension of the Woodward-Hoffmann methods requiring no symmetry) or a directly constructed correlation diagram show that a concerted passage from X=C + C=O to X=O and C=C is not forbidden (Figures 1 and 2). However, lower energy stepwise processes are not excluded, and the retention of stereochemistry in the alkene can be accommodated without presumption of a concerted process. Clearly, a more quantitative appreciation of the reaction surface is required. We chose to pursue CNDO estimates of the energy in order to determine the low energy path for these reactions. Calculations of the energy changes attending reaction of so complex a system as the Wittig betaine may be highly misleading if the geometry of each species along the reaction coordinate is not allowed to relax to its minimum energy. At the same time the size of the system (27 geometric parameters) and the number of variables which we wish to monitor (the distances between the heavy atoms) prohibit complete optimization of each parameter if a complicated function is chosen to represent the molecular energy. In this context the CNDO energy is a complicated function. The problem is to choose a geometry optimized in some very simple way before application of the CNDO method.

Geometry optimization of large systems has been given close attention by organic chemists<sup>11</sup> and more recently by physical biochemists.<sup>12</sup> If force constants for the several possible motions are available the Westheimer method<sup>13</sup> and its refinements become highly useful. Unfortunately the data are not complete for the systems in question, particularly for those configurations in which bonds are incompletely formed or broken.

(8) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 65-73.

(9) D. R. Kearns, *J. Amer. Chem. Soc.*, **91**, 6554 (1969).

(10) L. E. Friedrich and G. B. Schuster, *ibid.*, **93**, 4602 (1971), and references cited therein.

(11) J. E. Williams, P. J. Stang, and P. v. R. Schleyer, *Ann. Rev. Phys. Chem.*, **19**, 531 (1968).

(12) D. G. Brant, *Ann. Rev. Biophys. Bioeng.*, **1**, 412 (1972).

(13) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 12.

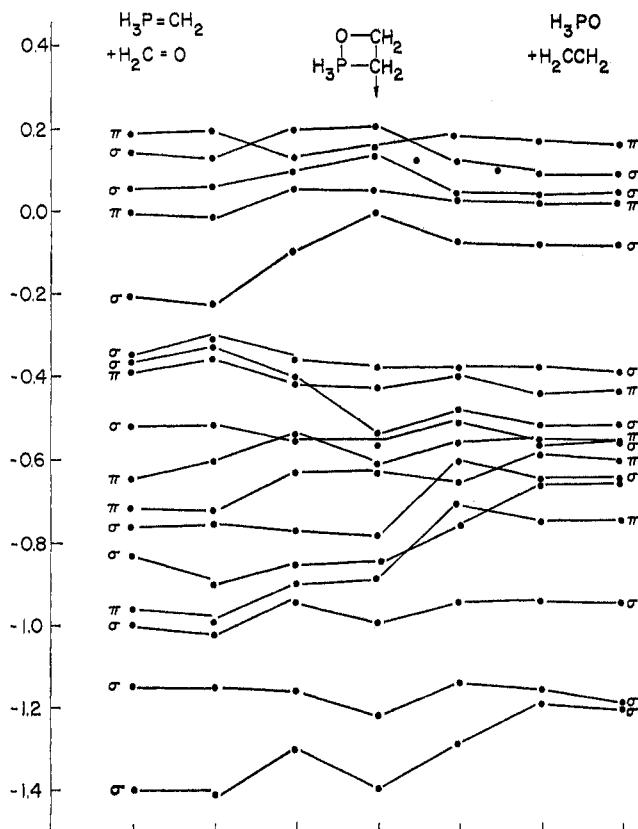


Figure 1.—Correlation diagram for conversion of methylene phosphorane and formaldehyde to ethylene and phosphine oxide via a dihydroxaphosphetane intermediate. The 13 doubly occupied bonding orbitals and the four lowest unoccupied orbitals are shown with the ordinate giving the orbital energy in atomic units. The abscissa describes the separation of the dihydroxaphosphetane to either starting materials or products. Because bonding orbitals of reactants correlate with bonding orbitals of products, the concerted process is allowed.

Geometric predictions based on point centers or repulsion are highly successful (Gillespie models for primary valence angles, "steric" models for long-range conformations) and can be refined by choosing point dipolar representations of heteronuclear bonds. In these models a careful appreciation of lone-pair effects is necessary for generally useful methods. However, if the configuration about atoms bearing lone pairs is immaterial or fixed by other considerations, angular geometries may be predicted merely by letting the nuclear repulsions be minimized. Our computation of the reaction paths of Chart I is composed of steps as follows: (1) choose a set of bond distances separating the heavy atoms; (2) find the angular arrangement which minimizes the repulsions among the nuclear cores; (3) perform the CNDO computation for that crudely optimized geometry.

Each of these stages requires comment. The choice of bond distances involves an assignment of bond lengths for bonds unbroken in the course of reaction, and a choice of the lengths of breaking bonds. The latter are the variables which define the energy surfaces we report and are varied in steps of 0.5 Å. The bond lengths of unbroken bonds are almost certainly altered in the course of these eliminations; for example, the C-C separation changes from a length typical of a single bond to a length typical of a double bond. This bond length contributes a substantial driving force

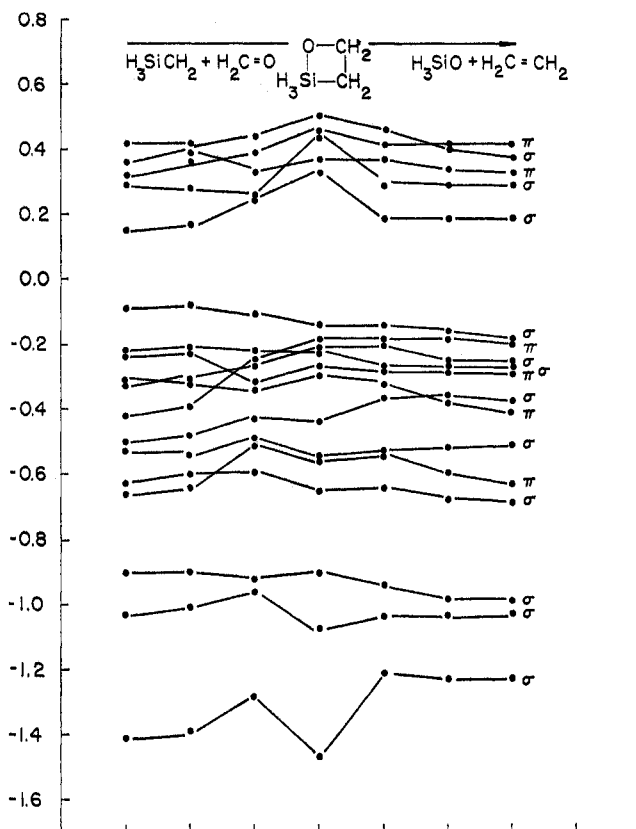


Figure 2.—Correlation diagram for conversion of silylmethyl anion and formaldehyde to ethylene and silanolate in a Peterson reaction. The diagram is constructed in a manner similar to that of Figure 1. The concerted process is allowed.

to the alkene formation which should not be neglected. However, for economic reasons we do not choose an optimum C-C bond length at each stage of the reaction but rather assign a fixed C-C bond length (Table I). This prejudice of our calculations must be kept in mind during the examination of the energy surfaces.

TABLE I  
BOND LENGTHS FOR FOUR-CENTER INTERMEDIATES **2a** AND **2b**

Bond	Length, Å	Bond	Length, Å
P-O	1.63	Si-O	1.63
C-C	1.54	C-C	1.54
C-H	1.09	C-H	1.09
P-H	1.44	Si-H	1.48
P-C	1.84	Si-C	1.89
C-O	1.44	C-O	1.42

The values chosen for the bond lengths of **2a** were idealized ones similar to those typically found for stable molecules and the geometry at phosphorus was assumed to be that of a trigonal bipyramid with the ring bonds apical to oxygen and equatorial to carbon.<sup>14</sup> The bond lengths of 1.63 Å for the apical P-O bond<sup>15</sup>

(14) D. E. Corbridge, *Top. Phosphorus Chem.*, **3**, 57 (1966).

(15) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Amer. Chem. Soc.*, **87**, 128 (1965).

and 1.44 Å for the C-O bond were selected rather than those reported for the stable oxaphosphetane **5b**, 1.79 and 1.36 Å, respectively.<sup>7b</sup> The stability of **5b** toward thermal fragmentation depends on the presence of the strongly electronegative trifluoromethyl substituents and is reflected by a rather long P-O bond and a short C-O bond. Use of this compound as a model would not appear to be so satisfactory as that of choosing more conventional bond lengths. This was also reinforced by the results of the calculations, which indicated an increase in the total energy of the molecule as either the P-O or C-O bond length was increased.

Minimization of the core repulsion with respect to all angular variables (presuming that bond lengths are fixed by other considerations) requires the scanning of a surface of 16 variables ( $3N - 6$  - number of bond lengths). Automation is of course essential and computer programs were employed for each of the problems of (1) varying angular features of the geometry only, and (2) systematically scanning the hypersurface defined by core repulsions. One of us (J.-T. H.) developed a program capable of varying the geometry by altering bond, torsional, and dihedral angles; a distinctive feature of this program is its ability to deal with ring systems. Rings may be constrained to be planar while being deformed in a plane or may be arbitrarily puckered. The scan of the surface was accomplished by a pattern search program STEPIT distributed by QCPE;<sup>16</sup> many of the optional abilities of STEPIT were removed for speed and compactness in this special application.

The CNDO computation was made possible by the program CNINDO distributed by QCPE<sup>16</sup> which can deal with second-row atoms bearing d orbitals. There seems to be a growing school of thought that d orbitals are not essential to the description of most chemical properties but do provide a convenient way to account for certain spectroscopic features of compounds containing second-row elements. We do not wish to maintain that d orbitals are a *sine qua non* in the Wittig and related systems but, noting that if d orbitals are suppressed it is often necessary to introduce excited p orbitals into the basis set, take the easy alternative and retain the d orbitals supplied by CNINDO. This algorithm may overestimate the population in d orbitals and may overstabilize the intermediate structures of trigonal bipyramidal geometry. CNINDO is known to underestimate strain energy and would overstabilize the crowded intermediate regardless of the use or refusal to use d orbitals. We will make some allowance for this source of error when we study the Wittig and Peterson surfaces.

**Decomposition of the Betaine Intermediate in the Wittig Reaction.**—For the purposes of analysis it is both convenient and instructive to prepare a three-dimensional potential surface for which the dihydrooxaphosphetane **2a** is the origin.<sup>17</sup> The vertical axis represents the energy calculated in atomic units for the species

(16) Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Ind. 47001.

(17) Three-dimensional potential surfaces have served as useful devices toward understanding the details of (a) elimination reactions, R. A. More O'Ferrall, *J. Chem. Soc. B*, 274 (1970), and (b) nucleophilic substitution reactions, E. R. Thornton, *J. Amer. Chem. Soc.*, **89**, 2915 (1967), and (c) have been suggested for reactions involving general acid-base catalysis, W. P. Jencks, *J. Amer. Chem. Soc.*, **94**, 4731 (1972); *Chem. Rev.*, **72**, 705 (1972).

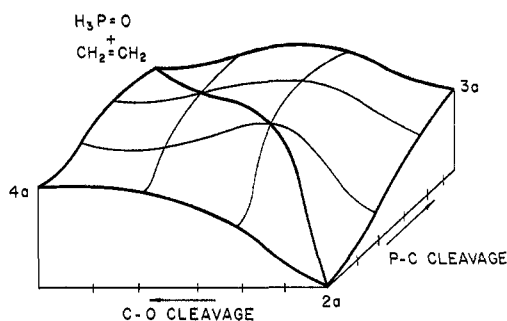


Figure 3.—Three-dimensional potential surface for conversion of a dihydrooxaphosphetane (**2a**) to ethylene and phosphine oxide.

which result when the internuclear separation between two atoms in **2a** is increased. The increase in internuclear separation in 0.5-Å increments is plotted along the two horizontal axes. Figure 3 shows the surface which is obtained when the reactions described by eq 5 and 6 are examined in this manner. The concerted decomposition of **2a** (eq 4) in which both the C-O and P-C bonds are equally stretched is then given by the energies which lie on the diagonal of the cube, while concerted reactions involving unequal C-O and P-C bond breaking are displaced from the diagonal toward the horizontal axes. Thus, Figure 3 depicts a continuum between the two limiting mechanisms expressed by eq 5 and 6 with the process expressed by eq 4 as the midpoint of that continuum.

The energies calculated for the limiting structures **1a-4a** are given in Table II. Simplification in this

TABLE II  
CALCULATED ENERGIES OF VARIOUS INTERMEDIATES IN  
WITTIG AND PETERSON ELIMINATION

Wittig		Peterson	
Species	Energy, atomic units	Species	Energy, atomic units
CH <sub>2</sub> O + H <sub>3</sub> PCH <sub>2</sub>	-42.6742	CH <sub>2</sub> O + H <sub>3</sub> SiCH <sub>2</sub> <sup>-</sup>	-39.9983
<b>1a</b>	-42.9183	<b>1b</b>	-40.3535
<b>2a</b>	-43.2832	<b>2b</b>	-40.4732
<b>3a</b>	-42.8706	<b>3b</b>	-39.9704
<b>4a</b>	-42.8000	<b>4b</b>	-39.8092
CH <sub>2</sub> CH <sub>2</sub> + H <sub>3</sub> PO	-42.8115	CH <sub>2</sub> CH <sub>2</sub> + H <sub>3</sub> SiO <sup>-</sup>	-39.9740

and all succeeding calculations is achieved by specifying all substituents on carbon and phosphorus as being hydrogen.

Of the three zwitterionic intermediates, the betaine **1a** is calculated to be the most stable. Using the conversion factor 1 atomic unit is equal to 621 kcal/mol along with experience from similar calculations that the energy differences are exaggerated by a factor of 3-4, the data indicate that **1a** is more stable than **3a** by 7-10 kcal/mol and that **3a** is more stable than **4a** by 11-15 kcal/mol. Therefore, if dihydrooxaphosphetane **2a** is an intermediate in this reaction, it should exhibit a greater tendency to revert to betaine **1a** than to go on to products *via* **3a** or **4a**. Of the paths which lead to products, that proceeding through **3a** is much preferable to that proceeding through **4a**, not only on the basis of the energies of the limiting structures but also because the energy calculated at various points along the reaction coordinates for each process favors P-C cleavage over C-O cleavage. Completely concerted decomposition of oxaphosphetane

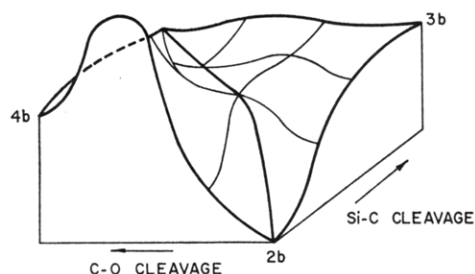


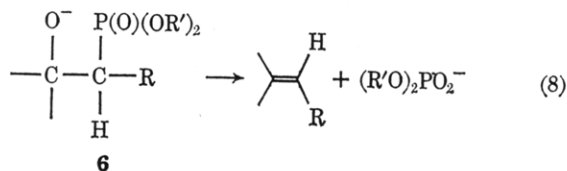
Figure 4.—Three-dimensional potential surface for conversion of a dihydrooxasiletanide anion to ethylene and silanolate.

**2a** is characterized by a rather steeply rising profile which reaches its maximum in potential energy at the point where each bond undergoing cleavage (P-C and C-O) has been stretched by *ca.* 1 Å. It would appear that the completely concerted process could only be favored if the second step of the competing stepwise process was disfavored. This is not borne out by the calculations, which indicate that only modest energy expenditures are required to convert **3a** (or **4a**) to products.

A significant portion of the stabilization calculated for the oxaphosphetane **2a** (66–89 kcal/mol more stable than **1a**) reflects the bias of the computational method toward condensed structures. While this figure is certainly much too high, the distinct depression in the potential surface does allow the conclusion that **2a** is a permissible and reasonable intermediate in these reactions.

We believe that the most general description for the decomposition of the betaine intermediate in the Wittig reaction is that which proceeds through an initial, reversible formation of a dihydrooxaphosphetane, which in turn undergoes fragmentation to olefin and phosphine oxide by a process in which cleavage of the phosphorus-carbon bond is considerably advanced over cleavage of the carbon-oxygen bond.

This analysis coincides well with certain experimental observations. For example, the base-catalyzed decomposition of  $\beta$ -hydroxyalkylphosphonate esters as shown in eq 8 is a key step in the Horner-



Wadsworth-Emmons modification of the Wittig reaction but occurs readily only when R is an effective carbanion-stabilizing substituent such as phenyl, cyano, or carboxy.<sup>1,18</sup>

The effect of such substitution in **6** is to stabilize the zwitterionic intermediate analogous to **3a** lowering the energies along the right side of the energy surface in Figure 3.

The inclusion of a degree of C-O cleavage concurrent with P-C cleavage provides a reasonable rationalization for the relative stability of **5**. The presence of two electron-withdrawing trifluoromethyl groups

(18) The implication of this observation with respect to the question of concertedness in decomposition of an oxaphosphetane intermediate was perceived and alluded to briefly in a footnote to a Communication to the Editor by E. J. Corey and G. T. Kwiatkowski, *J. Amer. Chem. Soc.*, **88**, 5654 (1966).

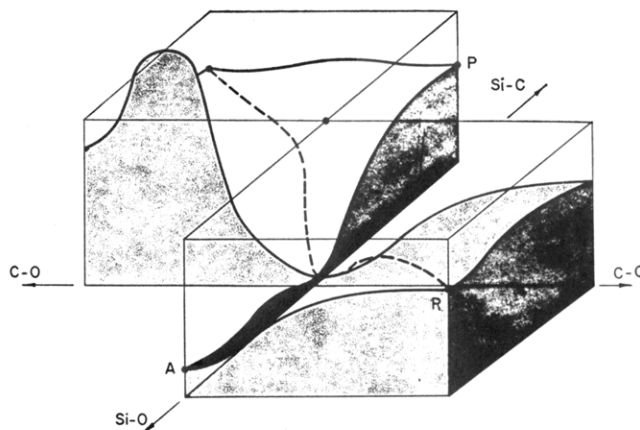
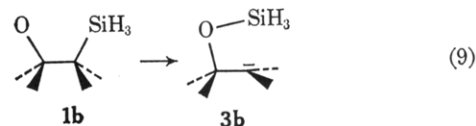


Figure 5.—A depiction of the potential surfaces for reaction of silylmethyl anion and formaldehyde (point R). Point A represents  $\text{H}_3\text{SiCH}_2\text{CH}_2\text{O}^-$  and point P represents  $^-\text{CH}_2\text{CH}_2\text{OSiH}_3$ . The four-center species **2b** is a shallow minimum along the path A to P.

on the carbon atom which is undergoing C-O cleavage serves to strengthen the C-O bond and raise the energy of the left side of the potential surface. An increase in P-C cleavage is therefore required to achieve the transition state.

**Decomposition of  $\text{H}_3\text{SiCH}_2\text{CH}_2\text{O}^-$  in the Peterson Olefination.**—A three-dimensional energy surface for the fragmentation of the hypothetical anionic dihydrooxasiletanide intermediate **2b** to ethylene and  $\text{H}_3\text{SiO}^-$  was constructed in a manner similar to that used for the Wittig reaction. This surface is shown in Figure 4 and is seen to be much more sharply skewed than that of the corresponding Wittig surface. In particular, cleavage of the C-O bond is characterized by a steep rise to an energy maximum of such magnitude as to be considered thermally inaccessible. The alternative mode which leads to products, cleavage of the Si-C bond, is much more favorable and suggests that Si-C cleavage is much more advanced than C-O cleavage in the transition state leading to olefin and silanolate. As in the Wittig case cleavage of the C-O bond subsequent to Si-C cleavage is a process of low energy and presumed to be rapid.

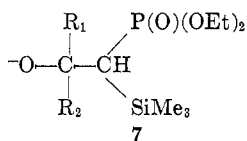
Another interesting and perhaps significant difference between the Wittig and Peterson surfaces is that formation of **2b** from **1b** (silicon case) is much less favorable than the corresponding formation of **2a** from betaine **1a** (phosphorus case). While **2a**, as determined by the calculations, is 66–89 kcal/mol more stable than **1a**, **2b** is only 18–25 kcal/mol more stable than **1b**. Given the bias toward condensed structures inherent in the calculations, this may mean that the dihydrooxasiletanide anion is bypassed as a true intermediate and may represent only an approximation of the transition state for conversion of **1b** to **3b** by nucleophilic attack of oxygen on silicon in an  $\text{S}_{\text{Ni}}\text{-Si}$  process (eq 9 and Figure 5).<sup>19</sup>



(19) For terminology and general discussion of reaction mechanisms at silicon see L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965.

The same dependence on the electron-withdrawing capacity of substituents exists here as in the Horner-Wadsworth-Emmons modification of the Wittig reaction mentioned in the preceding section. Elimination of silanolate from **1b** to yield olefin is complete within minutes below 25° when the carbon atom bearing the silicon (as trimethylsilyl) also bears a substituent capable of delocalizing negative charge such as phenyl, methylthio or phenylthio, phenylsulfinyl, 1,3-dithianyl, diethylphosphonate, and diphenylphosphino.<sup>2</sup> Elimination is demonstrably slower when electron-withdrawing substituents are absent. Many of the above substituents are not only carbanion stabilizing but also may be considered to stabilize a developing double bond in the transition state. It is clear that this latter factor cannot be important because it has been established with certainty that a sulfinyl substituent tends to destabilize a double bond directly attached to it.<sup>20</sup> If stabilization of the double bond were the only factor which determined ease of elimination, then vinyl sulfoxides would be formed with great difficulty. Such is not the case; vinyl sulfoxide formation takes place with great ease.<sup>21</sup> This behavior is in accord with the results of the calculations, which indicate extreme skewing of the energy surface toward **3b** capable of being stabilized effectively by substitution with electron-withdrawing groups.

Skewing of the energy surfaces depicted in Figures 3 and 4 toward **3a** and **3b** also provides a reasonable rationalization for the observation that intermediates like **7** which have the capacity to form vinylphospho-



(20) (a) D. E. O'Connor and W. I. Lyness, *J. Amer. Chem. Soc.*, **85**, 3044 (1963); (b) D. E. O'Connor and C. D. Broaddus, *ibid.*, **86**, 2267 (1964); (c) D. E. O'Connor and W. I. Lyness, *ibid.*, **86**, 3840 (1964).

(21) F. A. Carey and O. Hernandez, *J. Org. Chem.*, **38**, 2670 (1973).

nates by loss of  $\text{Me}_3\text{SiO}^-$  or vinylsilanes by loss of  $(\text{EtO})_2\text{PO}^-$  yield only the product from elimination of silicon. Stabilization of **3b** by  $-\text{P(O)(OEt)}_2$  is more effective than stabilization of **3a** by  $-\text{SiMe}_3$ , with the result that silicon migrates in preference to phosphorus.<sup>22</sup>

The tendency for silicon to migrate to oxygen in **7** because it leaves a more highly stabilized carbanion behind is sufficiently pronounced to overcome adverse steric effects when one of the R groups is isopropyl and the other hydrogen. The only products are the corresponding cis and trans diethyl vinylphosphonates with the cis predominating by 2.4:1.<sup>2c</sup> If a close balance existed between silicon migration and phosphorus migration a reasonable presumption would have been for stereoselective formation of a mixture of *trans*-vinylsilane and *trans*-vinylphosphonate.

In summary, the Peterson reaction differs from the Wittig reaction in that the four-center array represents, at most, an unstable intermediate during the passage of **1b** to **3b**. The preferential loss of  $\text{Me}_3\text{SiO}^-$  in species such as **7** results not so much from an intrinsically greater "migratory aptitude" on the part of silicon as from the greater stabilizing effect of phosphonate on the resulting carbanion.

**Registry No.**—**1a**, 16247-01-1; **1b**, 40110-49-4; **2a**, 40110-50-7; **2b**, 40330-42-5; **3a**, 20502-84-5; **3b**, 40110-53-0; **4a**, 40110-52-9; **4b**, 40140-15-6.

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(22) Quantitative data are not available on the relative carbanion-stabilizing abilities of  $-\text{SiMe}_3$  and  $-\text{P(O)(OEt)}_2$  but it seems likely that such data would coincide with expectation. In this context it is noteworthy that metalation of diethyl methylphosphonate occurs much more readily than metalation of tetramethylsilane; see ref 18 and D. J. Peterson, *J. Organometal. Chem.*, **9**, 373 (1967).